AD-A152 288

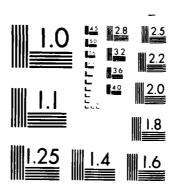
CEMENT COMPOSITION AND CONCRETE DURABILITY IN SEA MATER
(U) ARMY ENGINEER MATERIARYS EXPERIMENT STATION
YICKSBURG MS STRUCTURES LAB A D BUCK ET AL. DEC 84
MES/TR/SL-84-21

F/G 11/2

NL

END
NAME

END
NAM



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS 1963. A

US Army Corps of Engineers



## CEMENT COMPOSITION AND CONCRETE DURABILITY IN SEA WATER

by

Alan D. Buck, Katharine Mather, Bryant Mather Structures Laboratory

DEPARTMENT OF THE ARMY Waterways Experiment Station, Corps of Engineers PO Box 631 Vicksburg, Mississippi 39180-0631



December 1984 Final Report

Approved For Public Release Distribution Unlimited



Prepared for DEPARTMENT OF THE ARMY US Army Corps of Engineers Washington, DC 20314-1000

Under Civil Works Investigation ES Item 603.1



### REPRODUCED AT GOVERNMENT EXPENSE

The contents of this report are not to be used for advertising, publication, or promotional purposes. Citation of trade names does not constitute an official endorsement or approval of the use of such commercial products.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Destroy this report when no longer needed. Do not return it to the originator.

SETURITY CLASSIFICATION OF THIS PAGE (When Date Entered)

REPORT DOCUMENTATION	PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1 REPORT NUMBER	2. GOVT ACCESSION NO.	3 RECIPIENT'S CATALOG NUMBER
Technical Report SL-84-21	AD-A152288	
4 TITLE (and Subtitle)	<del>4 1 1 1 1 1 1 1 </del>	TYPE OF REPORT & PERIOD COVERED
CEMENT COMPOSITION AND CONCRETE DU	JRABILITY IN	i ;
SEA WATER		Final report
	ļ	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(a)		8. CONTRACT OR GRANT NUMBER(4)
Alan D. Buck		
Katharine Mather		
Bryant Mather 9. PERFORMING ORGANIZATION NAME AND ADDRESS		10 DOCCOME ELEMENT PROJECT TASK
US Army Engineer Waterways Experim	ment Station	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
Structures Laboratory		Civil Works Investigation
PO Box 631, Vicksburg, Mississippi	39180-0631	ES Item 603.1
11. CONTROLLING OFFICE NAME AND ADDRESS		12. REPORT DATE
DEPARTMENT OF THE ARMY US Army Corps of Engineers		December 1984
Washington, DC 20314-1000		13. NUMBER OF PAGES
14 MONITORING AGENCY NAME & ADDRESS(II differen-	t from Controlling Office)	15. SECURITY CLASS. (of this report)
		Unclassified
		15a. DECLASSIFICATION DOWNGRADING
		SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)		
Approved for public release; distr	ribution unlimite	ad.
improved for public release, discr	Ibacion antimize	
17. DISTRIBUTION STATEMENT (of the abetract entered	in Block 20, if different fro	om Report)
18. SUPPLEMENTARY NOTES	<del></del>	
Available from National Technical	Information Serv	vice, 5285 Port Royal Road,
Springfield, Virginia 22161.		•
19. KEY WORDS (Continue on reverse side if necessary an	id Identify by block number)	)
Concrete research (LC)		Sea-waterAnalysis (LC)
ConcreteAdditivesTesting (LC	;)	
Cement (LC) Alkali-aggregate reactions (LC)		
Sulphate-resistant concreteTest	ing (LC)	
20. ABSTRACT (Continue en reverse side if necessary and		
		litu of concrete in one voter
were investigated. The separate a		lity of concrete in sea water sets of alkali-silica reaction
and sulfate attack were evaluated		

specimens from 16 mixtures exposed in warm sea water at St. Augustine, Florida.

Three mixtures were made that were susceptible to both alkali-silica reaction and sulfate attack, three that should not manifest either reaction,

### SECURITY CLASSIFICATION OF THIS PAGE(When Data Entered)

### 20. ABSTRACT (Continued).

three susceptible to alkali-silica reaction only, and seven susceptible to sulfate attack only. Performance of specimens in the field plus some laboratory tests indicated these intents were generally successful. A major finding from this work was that the combined effects of both reactions caused quicker and more complete destruction of concrete and mortar than either reaction alone. While one would intuitively guess this would be the case, this work provided proof of this for the first time, so far as is known. Another result was to confirm that the mitigating effects of a pozzolan are optimized when the proper amount of pozzolan is used. This work also showed more alkali-silica reaction due to high potassium levels than to high sodium levels.

### **PREFACE**

The work described in this report was authorized in 1954 and started in 1955; it involved laboratory work and exposure of concrete specimens at St. Augustine, Florida; it was part of Engineering Study Item 603.1.

Mr. Fred Anderson (DAEN-CWE-DC) was the OCE Technical Monitor when this report was prepared.

Many people were involved in this project over this span of time.

Mr. Cecil Willetts was the original Project Leader and Mr. Alan D. Buck was the last Project Leader. All of the laboratory work was done in the Structures Laboratory (SL). Original overall supervision was under Mr. T. B. Kennedy; final supervision was under Mr. John M. Scanlon, Chief, Concrete Technology Division, and Mr. Bryant Mather, Chief, SL. The report was prepared by Mr. Buck.

Commanders and Directors of the USAE Waterways Experiment Station (WES) during preparation and issuance of this report were COL Tilford C. Creel, CE, and COL Robert C. Lee, CE. Mr. F. R. Brown was Technical Director at this time.

20013	Hen For	
PI	781	K
: :	i d ustte <b>n</b> ∠	
<i>i</i>		
1000	-Cutton/	
1 . 2	lability.	dones
	Aged L. Ale	1/or
$\mathbf{D}^{\pm}$ , $\epsilon$	ું ફુપલ દુવસ	
AI		
HI		



### Contents

	Page
Preface	1
Conversion Factors, Non-SI to SI (Metric) Units of Measurement	3
Background	4
Materials, Mixtures, and Tests	5
Materials	5 6
Results	7
Sea water	7 7 8
Concretes	9
Discussion	10
Conclusions	11
References	13
Figures 1 and 2	
Tables 1-9	
Six Inclosures (Patrographic Reports)	

# Conversion Factors, Non-SI to SI (Metric) Units of Measurement

Non-SI units of measurement used in this report can be converted to SI (metric) units as follows:

Multiply	<u>by</u>	To obtain
inches	25.4	millimetres
angstroms	0.1	nanometres
pounds (force) per square inch (psi)	6.894757	kilopascals
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*

<sup>\*</sup> To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To obtain Kelvins (K) readings, use: K = (5/9)(F - 32) + 273.15.

### CEMENT COMPOSITION AND CONCRETE DURABILITY IN SEA WATER

### Background

- 1. A study to determine if sulfate attack of concrete would have any effect on the degree of alkali-silica reaction that developed in the same concrete was conceived and executed. Laboratory tests were used to characterize the materials used and to evaluate their potential for expansive reaction or reactions when they were used in various combinations. Field exposure and testing were used to evaluate 16 different concrete mixtures. Concrete specimens were made in the laboratory and most of them were transported to the warm sea water exposure station at St. Augustine, Florida; the balance of the concrete specimens were stored out of doors at the moderate weathering exposure station near Jackson, Mississippi. The concrete specimens were monitored periodically by determination of pulse velocity and by visual inspections for about 10 years. When specimens failed, some of these were returned to the laboratory for petrographic examination. The results of this testing have had only limited publication. 1,2 The intent of this work was to provide opportunity for alkalisilica reaction or sulfate attack or both to occur in a favorable environment (warm sea water) and to monitor the results.
- 2. Specimens representing these 16 concrete mixtures were installed at the mean-tide level at St. Augustine, Florida, in 1955-56. The mixtures involved combinations of four portland cements, two granulated iron blast-furnace slags, three aggregates, and two types of pozzolan (fly ash and ground calcined shale). The four portland cements included examples with high- and low-alkali contents and high- and low-tricalcium aluminate contents. The aggregates included reactive and nonreactive types. Three of the mixtures with high-alkali, high-C<sub>3</sub>A cement, and reactive aggregate were expected to experience both alkali-aggregate reaction and sulfate attack; three others with high-alkali, low-C<sub>3</sub>A cement, and reactive aggregate were expected to experience only alkali-aggregate reaction; seven with nonreactive aggregate but high-C<sub>3</sub>A cement were expected to experience sulfate attack only; the remaining three were not expected to experience either kind of attack. Since two of the mixtures were made twice, there was a total of 18 mixtures with 16 of them being different.

3. A description of this project and discussion of results to that time were presented at the 1959 American Concrete Institute (ACI) Convention.  $^6$ 

### Materials, Mixtures, and Tests

### Materials

4. The four portland cements used are shown below:

RC No.	Alkali	Tricalcium Aluminate (C3A*)
331	High	Low
332	High	High
333	Low	Low
334	Low	High

<sup>\*</sup> Usual cement noation,  $C_3A = 3Ca0 \cdot Al_2O_3$ 

5. The two pozzolans and the two ground granulated iron blast-furnace slags that were used are shown below:

Serial No.	Type of Material	Portland Cement Replacements by Solid Volume, %
AD-3(3)	Fly Ash	20
AD-5(3)	Calcined Shale	30
RC-216(4)	Granulated Blast- Furnace Slag	40
RC-296	Granulated Blast- Furnace Slag	40

6. The aggregates that were used included:

CL Serial No.		f Aggregate Material	Relative Alkali- Silica Reactivity
VICKS-3 G-1(20) VICKS-3 MS-10	Coarse Fine	Crushed Dolomitic Limestone	None
WES-1 G-5(3) WES-1 S-8(3)	Coarse Fine	Natural Siliceous Gravel and Sand	Moderate

CL Serial No.	Kind of Aggregate and Material	Relative Alkali- Silica Reactivity
OM-2G-2(9)	Coarse Quartzite	Highly
CRD-G-22(2)	Fine Pyrex Glass	Highly

- 7. The quartzite was reactive because it contained an opal matrix; the quartzite was used to replace 5 percent of the natural gravel in some mixtures. When the natural gravel was crushed for use in mortar bars, the quartzite replacement was 1, 3, and 1 percent of the 600-µm, 300-µm, and 150-µm (No. 30, 50, and 100) sizes, respectively. When the replacement of natural gravel was in concrete, the replacement with quartzite was by solid volume of the total gravel with approximately 35 percent in the 19.0-mm to 37.5-mm (3/4- to 1-1/2- in.) size when used and the balance in the 4.75-mm to 19.0-mm (No. 4 to 3/4-in.) size material.
- 8. The limestone, natural sand and gravel, and the quartzite, in different combinations, were used in the concrete. The Pyrex glass was used only in two of the laboratory mortar mixtures. These Pyrex mixtures were repeated for a total of four mixtures.

### Mixtures and tests

- 9. Various physical and chemical tests and petrographic examinations were used to characterize the materials and some of the mortar mixtures that were made. This included petrographic examination of some concrete specimens from storage at St. Augustine. Specimens stored out of doors at Jackson were inspected as well as being tested in conjunction with testing of the St. Augustine specimens.
- 10. Concretes. In 1955, three rounds of 12 mixtures were made. Three concrete beams, each 6 by 6 by 30 in., and nine 6- by 12-in. cylinders were made from each round for a total of 108 beams and 324 cylinders. Six beams from each mixture were placed on the exposure rack at St. Augustine, Florida, in August 1955, and the remaining beams were placed outdoors at the CL in September 1955.
- 11. In 1956, three rounds of six more concrete mixtures were made as before. Six beams from each mixture were placed at St. Augustine and the remaining three from each mixture were placed outdoors at the CL, all in August 1956. Two of these were repeats of the earlier mixtures but with 19.0-mm (3/4-in.) instead of 37.5-mm (1-1/2-in.) nominal maximum aggregate size.

- 12. The pulse velocity and dynamic Young's modulus of elasticity (E) of the beams kept at St. Augustine and outdoors in Mississippi were determined biennially until 1970. In mid-1971, one concrete beam from each of the 15 sets that had not failed at St. Augustine was returned to the laboratory and given a final reading. These included beams 1833, 1842, 1863, 1868, 1878, 1889, 1901, 1905, 1917, 2542, 2545, 2554, 2565, 2571, and 2587. No readings of the specimens kept outdoors in Mississippi were made after the 1970 reading.
- 13. The cylinders were tested for static E at 28 and 90 days and for compressive strength at 7, 28, and 90 days.
- 14. All of the 18 concrete mixtures had a water-cement ratio of 0.5, slump of  $2-1/2 \pm 1/2$  in., and air content of 5 + 1/2 percent.
- 15. Mortar. A total of 16 mixtures were made and the bars were tested for length change by CRD C  $123-48^3$  (ASTM: C 227). Fourteen of the mixtures were different combinations of materials and two mixtures were repeats.
- 16. Ten mortar mixtures were made and specimens were measured for length change by the Lerch test  $(CRD-232)^3$  (ASTM: C 452) and six other mixtures by the Lean Mortar Bar Test\* to evaluate the sulfate resistance of the four project cements and of the two high  $C_3A$  ones (RC-332, 334) when combined with granulated blast-furnace slag.

### Results

### Sea water

17. A chemical analysis of a sample of sea water from St. Augustine was made in 1958; the data are shown in Table 1. The temperature of the sea water was  $82^{\circ}$  F when this sample was taken.

### Project Materials

18. Tables 2, 3, and 4 contain data for the four cements, two ground slags, two pozzolans, and five aggregates, respectively. The most notable features of the cements are their range in  ${\rm C_3^A}$  and total alkali contents and distribution of alkalies. These are:

<sup>\*</sup> Done as described in Appendix A to the 1952 report of ASTM Committee C-1, ASTM Proceedings, Vol 52.

			Alkali as
Cement RC-	Calculated C <sub>3</sub> A	Total Alkali as Na <sub>2</sub> 0	$K_2O Na_2O$
331	5	0.94	0.23 0.79
332	14.3	1.00	0.95 0.37
333	3	0.33	0.20 0.20
334	13.5	0.24	0.16 0.13

- 19. Inclosure 1 is a 1955 petrographic report about the five aggregates (three types) that were used in the concrete mixtures. It points out that the Klufa quartzite contained about 14 percent opal. Since the quartzite was used at the 5 percent level when it was used, there should have been about 0.7 percent opal in the total aggregate. This is a probable pessimum which was confirmed by field behavior of appropriate beams (Table 9).
- 20. Inclosure 2 is a petrographic report, largely X-ray diffraction (XKD), of cements RC-332 and 334 and of two slags from the same sources as the two project slags. It points out that while both cements are high  $\rm C_3A$  by calculation, based on the chemical analyses, RC-334 has about half as much crystalline  $\rm C_3A$  by XRD. The difference in these two cements and their sulfate resistance was discussed extensively in a 1965 report. At that time it was concluded that since they were similar in calculated  $\rm C_3A$  content but differed significantly in amount of crystaline  $\rm C_3A$  by XRD, the difference was that some of the  $\rm C_3A$  was glassy and that this explained their differing behavior to sulfate attack. The slags are shown to be largely glassy with small amounts of crystalline quartz, calcite, and melilite (RC-216(4) only).
- 21. Mortars. Table 5 shows expansion data through 1 year for the 16 mortar mixtures. No bars were made with the low-alkali and high- $C_3A$  cement RC-334. The chert gravel and opaline quartzite combination with high-alkali cement RC-331 was repeated with substantially more expansion the second time. Since this testing was done when there was difficulty in obtaining the nearly 100 percent relative humidity within a container that is required for this test, the presumption is that the humidity was lower in the initial test. The same aggregate combination with the other high-alkali cement (RC-332) was also repeated, both sets of results were similar so humidity was not a problem. Note that expansion with high-alkali and high  $C_3A$  RC-332 was approximately twice what it was with high-alkali and low  $C_3A$  cement RC-331.
- 22. Inclosure 3 is a petrographic report about examination of 12 of the 16 mortar bar sets (Table 5) after testing was stopped after 1 year. This

0.01.10.

Compressive Strength and Static Modulus Additional 18 Congrete Mixtures

	Mixture Data		soudary)	11vg St	rength,	Static	Static Modulus,
Designa- tion(a)	Materials		7 par	7 Day 28 Day 90 Day	90 Day	28 Day	90 Day
		Low-Alkali, Low-C <sub>3</sub> A Genent RC-333	W-C 3A Cem	ent RC-	333		
. <b>.</b>	aggregate 5 noregat	on on the state of	2790	3910	5210 4590	4.90	5.44
.1	i dinasarad	High-Alkali, Low-C <sub>3</sub> A Cement RC-331	Low-C <sub>3</sub> A Ce	ment RC	-331 		
۱~	Natural aggregate		2740	3850	7,00	5.48	5.42
. ~		quartzite	2700	3860	4450	5.35	6.22
10	+ 5 percent	quartzite,	2360	3520	4360	5.50	5.92
Ð		uartzite, shale	1970	3360	4450	4.88	5.22
		Low-Alkali, Hi	$High-C_3A$ Cement RC-334	ement RC	-334		
9	stone		2950	4070	5010	5.18	5.35
<b>a</b>	stone		3190	4690	2460	5.20	0.0 10.0
ជ	Limestone aggregate, RC-296 slag	40 percent	7360	3870	0664	, C . C	7.71
ſ±.	stone -216(	40 percent	2300	4150	5100	5.35	5.61
		High-Alkali,	High-C <sub>3</sub> A C	Cement R	RC-332		
5	Limestone aggregate		3630	7400	4870	5.05	5.14
Y	a)		3750	4200	7690	5.46	5.56
∞	Natural aggregate		2920	3800	4100	27.0	0.31
4	aggregate +	5 percent	3080	3970	4300	5.56	5.33
12	quartzite Natural + 5 percent quartzite 20 percent fly ash (AD-3(3)	quartzite, ı (AD-3(3))	2610	3650	4190	5.43	5.88

Table 7

# Selected Length-Change Data for Six Mortar Mixtures by the Lean Mortar-Bar Test (a)

Materials	14 Day	28 Day	Expansi 84 Day	Expansion, %(b) 14 Day 28 Day 84 Day 196 Day 364 Day	364 Da	
RC-332 (High alkali, high $C_3A$ ) RC-332 plus 40 percent RC-216(4) slag	0.008 0.010	0.008 0.027 ( 0.010 0.024	(Bars b 0.032	(Bars broke after 42-day reading) 0.032 0.042 0.057 0.104 (448	<u>.</u>	42-day 0.057
RC-332 plus 40 percent RC-296 slag	0.009	0.020	0.027	0.036	O	0.058
RC-334 (Low alkali, high $C_3A$ )	0.013 0.03 day reading)	0.013 0.051 lay reading)		0.160 1.235 (Bars broke after the	(Bar	s bro
RC-334 plus 40 percent RC-216(4) slag RC-334 plus 40 percent RC-296 slag	0.009	0.009 0.022 0.008 0.019	0.028	0.036	0	0.043

days) days)

196-

days) days)

The method used was referenced as a footnote in the report. Each value is an average, usually of four bars. (a)

Table 6

Selected Length-Change Data of 10 Mortar Mixtures by the Lerch Added Sulfate Test (CRD-C 232) (a)

		Expa	Expansion, %(D)(C)		
	7 Dav	28 Day	28 Day 84 Day	196 Day	364 Day
Materials					
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	0.024	0.047	0.073	0.094	0.108
$RC-331$ , figh airais, tow $3^{23}$			0	0,0	756
and the state of the Cab	0.051	0.124	0,346	0.240	1000
KC-332, High aikaii, IIIBII oga	0.040	0.105	0.268	0.269	0.272
Repeat of above mixture	870 0	0.117	0.222	0.222	0.224
RC-332 plus 40 percent RC-296 slag	0.0	0 133	0 155	0.158	0.157
RC-332 plus 40 percent RC-216(4) slag	0.049	0.133	001.0	)	
	0.013	0.025	0.036	0.044	0.056
RC-333. Low alkali, low C,A	0.013	0.020	•		
	750	0 142	0.354	1.762	1.772
RC-334, Low alkali, high C3A	10000	0.142	200.0	1 312	1,332
The state of the s	0.051	0.130	0.437	710.1	
Repeat of above mixture	0.057	0.115	0.228	0.331	0.333
RC-334 plus 40 percent RC-490 stak	7500	0.126	0 228	0.246	0.250
RC-334 plus 40 percent RC-216(4) slag	0.00	0.140			

Reference 1. Each value is an average, usually of six bars. All values are positive. (C) (B) (B)

Table 5

Selected Length-Change Data of Bars from 16 Mortar Mixtures in the Alkali-Aggregate Test for Reartivity (CRD-C 123) (a)

				Expa	Expansion, $%(b)(c)$	(p)(c)	
Cement RC-	Aggregate	Pozzolans	3 Day	28 Day	84 Day	196 Day	364 Day
331	Limestone Sand	None	-0.005	-0.005	0.000	0.005	0.008
331	Natural Sand	None	-0.004	-0.003	0.001	000.0	0.007
High-Alkali							
Low C3A							
331	Gravel	None	-0.001	-0.002	-0.001	-0.003	0.000
331	Gravel + Quartzite	None	0.001	0.004	0.011	0.010	0.014
	Repeat of Above Mixture		0.001	0.014	0.025	0.054	0.063
331	Pyrex Glass		0.075	0.257	0.321	0.344	0.358
331	Gravel + Quartzite	AD-5(3)	0.003	-0.003	-0.003	-0.002	0.004
331	Gravel + Quartzite	AD-3(3)	0.002	0.003	0.010	0.013	0.020
332	Gravel + Quartzite	None	0.012	0.022	0.069	0.120	0.130
High-Alkali							
High C <sub>3</sub> A							
	Repeat of Above Mixture		0.010	0.028	0.070	0.105	0.109
332	Pyrex Glass		0.161	0.288	0.298	0.311	0.320
332	Gravel + Quartzite	AD-5(3)	0.005	0.003	0.003	0.003	0.009
333	Gravel + Quartzite	None	0.001	-0.003	-0.002	-0.004	0.000
333	Limestone Sand	None	-0.002	-0.006	-0.003	-0.003	000.0
Low Alkali							
Low C <sub>3</sub> A							
333	Natural Sand	None	-0.001	-0.004	0.001	0.000	0.002
333	Gravel	None	0.001	-0.001	000.0	-0.008	-0.003

Reference 1; the test method was deviated from fixed proportions so the water content of each mixture (b) would give a flow of 110 + 5 percent.
(c) Each value is the average of nine bars.

All values are positive unless preceded by a minus sign.

Table 4 Physical Data for Coarse and Fine Aggregates

	WES-1 G-5(3)	6-5(3)		VICKS-3	VICKS-3 G-1(20)		0M-2	OM-2 G-2(9)	
	Variors	Gravel		Limes	tone		(Juar	tzite	
	10 0 mm to	4 75 mm +0		19.0 mm to	4.75 mm to		19.0 mm to	4.75 mm to	
	27 5 27	19 O mm		37.5 mm	19.0 mm		37.5 mm	19.0 mm	
	(3/4 to	(No. 4 ro	WES-1 S-8(3)	(3/4 to	(No. 4 to	VICKS-3 MS-10	(3/4 to	(No. 4 to	
	1-1/2 in.)	3/4 in.)	Natural Sand	1-1/2 in.)	3/4 in.)	Limestone Sand	1-1/2 in.)	3/4 in.)	
(a) (a) (b) (a) (b) (b) (b)	2.56	2.50	2.62	2.70	2.71	2.66	2.37	2.36	
sp. cr., sat. suit. bry	2.5	7.5	0.5	9.0	0.5	1.5	2.2	2.4	
ption, s'''' (a)	? -		}	7.6	10.7	i	7.0	15.4	
Flat and Elongated, % (a)	 	1.7	2.2	7 6	5.9	14.0	8.9	12.8	
45504 Loss, % (Weighted AVR) Abrosion Lose (1.A.), %(a)	21.7 24.5	24.5	; ;	27.1	25.4	1	30.8	30.0	
Grading (Cum. % Passing)(a)							001		
mm (2 in.)	100						100		
37.5 mm (1-1/2 in.)	86			100			0 7	001	
0 mm (1 in.)	56	100		52	001		ور د	96	
0 mm (3/4 in.)	01	96		,	80 (		2 -	0, 7	
5 mm (1/2 in.)	~	70		2	/9		٦ ٥	O 00	
mm (3/8 in.)	0	87		5	£43		> 0	<b>.</b>	
5 mm (No. 4)	0	2	95	0	<b>x</b> 0	00.0	>	<b>-</b>	
6 mm (No. 8)			81			56,			
8 mm (No. 16)			70			00			
m (No. 30)			54			30			
m (%o. 50)			17			07			
, _m (No. 100)			•			07			
.m (No. 200)			3.2			7.0			
assing 75 µm (No. 200)			2.7			). v			
ineness Modulus			9/.7			20.2			

(a) Reference 1.

Table 3 Chemical and Physical Data for Four Admixtures

	AD-3(3)	AD-5(3)	RC-216 Granulated Blast-Furnace	RC-198 Granulated Blast-Furnace
Chemical Data,	LV ASH	Calcined Shale	37 9	Stag Co.
31.2 A1.0,	14.7	11.8	13.3	11.3
5 3 Fe <sub>3</sub> 0 3	18.9	6.4	1.0	0.5
CaO	8.5	9.2	35.3	43.6
ояк	2.1	2.9	10.2	2.0
SO	3.0	0.4	0.1	0.1
Loss on Ignition	1.4	8.9	9.0	1.4
Na,0	2.5	0.2	0.2	0.2
1 O . X	2.0	7.0	1.0	1.2
Fotal Sulfur	0.2	7.0	1.3	6.0
Insoluble Residue	66.4	66.1	0.5	9.0
iotal Carbon	6.3	1.1	0.5	0.4
Physical Data, Z				
Air-permeability Fineness, cm <sup>2</sup> /g (Blaine)	3580	12,930	3700	3600
Amount Passing 45-um (No. 325) sieve	7.76	7.76	97.2	90.2
Specific dravity	2.52	2.50	2.87	2.84

Data from WES MP No. 6-123, Investigation of Cement-Replacement Materials, Report No. 1, Apr 1953. Same source as the RC-296 that was used in this work. (a) (b)

Table 2 Chemical and Physical Data for Four Portland Cements

		000	BC-333	788-Da
	RC-331	KC-332	Tota Alkali	Low Alkali
	High Alkall, Low C <sub>2</sub> A	High C <sub>3</sub> A	Low C <sub>3</sub> A	High C <sub>3</sub> A
Chemical Data, &	7.77	19.6	24.5	21.6
5102	1 7 7	α ν	3.0	5,5
$^{A1}_{2}^{20}_{3}$	j j	2		-
Fe <sub>2</sub> 0 <sub>2</sub>	4.2	2.5	2.9	1.9
CaO	63.7	63.1	64.2	63.0
Ago	1.1	2.7	1.0	2.9
SOS	2.0	2.1	2.1	2.1
Loss on Ignition	1.0	1.4	6.0	1.4
Na. O	0.79	0.37	0.20	0.13
- 2 0 2	0.23	0.95	0.20	0.16
7. Total Alkalies as Na,0	0.94	1.00	0.33	0.24
Z Insoluble Residue	0.3	0.3	0.2	0.3
Calculated Compounds, %				
ຮ່ວ	20	52	45	97
S, C, S	26	17	36	27
2 C.A	5	14.3	3	13.5
$_{ m C_4AF}$	13	∞	6	9
Physical Data				
Air-permeability Fineness, cm <sup>2</sup> /g (Blaine)	3005	3290	3240	3550
Specific Gravity	3.15	3.14	3.16	3.10
Compressive Strength, psi				
3 days	2620	2510	1820	1700
7 days	3450 5600	3740 4600	2850 4420	7840 4840

Table 1

Analysis of Sea Water from St. Augustine Exposure

Station, Made by Chemistry Section, CD

Reported 9 September 1958

Constitu	ients	ppm	Equivalents
Suspended	Solids	160.0	
Dissolved	Solids	38,610	
Dissolved	$SiO_2$	6.0	
Dissolved	R <sub>2</sub> O <sub>3</sub>	7.0	
Dissolved	Ca	430,2	21.46
Dissolved	Mg	1,340.0	110.2
Dissolved	Na	11,130	484.1
Dissolved	K	447	11.43
			627.19
Dissolved	C1	20,460	576.9
Dissolved	so <sub>4</sub>	2,780	57.88
			634.78
	<del> </del>		

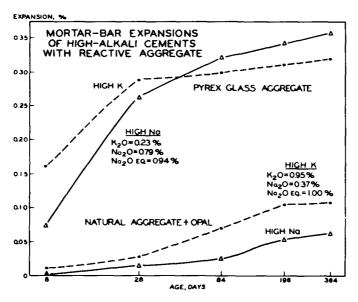


Figure 1. Mortar-bar expansions of high-alkali cements with reactive aggregate

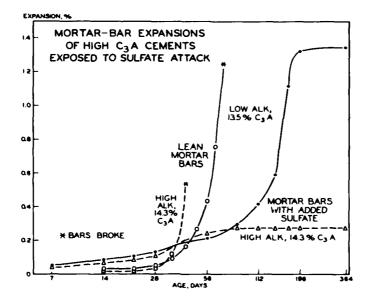


Figure 2. Mortar-bar expansions of high-C<sub>3</sub>A cements exposed to sulfate attack

### References

- "Investigation of Performance of Concrete and Concreting Materials Exposed to Natural Weathering," Section 29 of Vol I, Active Investigations, Vol 2, Completed Programs of Investigation, with periodic supplements, U. S. Army Engineer Waterways Experiment Station, CE, Technical Report No. 6-553, Vicksburg, Miss., Jun 1960.
- 2. Mather, Katharine, "Concrete Weathering at Treat Island, Maine," pp 101-111, ACI SP-65, Performance of Concrete in Marine Environment, 1980.
- 3. U. S. Army Engineer Waterways Experiment Station, CE, <u>Handbook for Concrete</u> and Cement, with quarterly supplements, Vicksburg, Miss., Aug 1949.
- 4. Mather, Bryant, "Investigation of Portland Blast-Furnace Slag Cements," Report 2, Supplementary Data, U. S. Army Engineer Waterways Experiment Station, Technical Report No. 6-445, Sep 1965, Vicksburg, Miss.
- 5. U. S. Army Engineer Waterways Experiment Station, Technical Report No. 6-481, "Effectiveness of Mineral Admixtures in Preventing Excessive Expansion of Concrete Due to Alkali-Aggregate Reaction," Jul 1958, Vicksburg, Miss.
- 6. Mather, Bryant, 1959, "Cement Composition and Durability in Sea Water," American Concrete Institute Convention, Feb 1959, presentation at off-the-record Research Session (not published).

36. Two cements (RC-332, 334) with similar high amounts of calculated  ${\rm C_3A}$  but different amounts of crystalline  ${\rm C_3A}$  by XRD reacted differently to sulfate attack. The one with more glassy aluminate (RC-334) showed more and longer-term expansion as if the glassy phase was slower to react; perhaps because it was combined with other more slowly reactive phases.

that should show the effects of alkali-silica reaction only, and seven mixtures showing the effects of sulfate attack only. Armed with a knowledge of the materials used and consideration of the test results that have been described, it is apparent that this intent was generally successful. The mitigating effect of different pozzolans or slags on these reactions was recognizable. However, since they were not necessarily used at their optimum amounts, the effects were often limited in scope or duration.

- 31. Due to the fact that the two high-alkali cements (RC-331, 332) differed in type of major alkali, sodium or potassium, as well as being low or high in  $C_3A$ , comparisons between the effects of these cements was never definitely as simple as being due to  $C_3A$  or to type of alkali. However, comparison did indicate that the higher potassium cement (RC-332) did cause more and quicker expansion due to alkali-silica reaction than did the higher sodium cement (RC-331). This is shown graphically in Figure 1 which was used in the 1959 presentation at the ACI Convention.
- 32. The use of XRD to show that two high- ${\rm C_3A}$  cements (RC-332, 334) of presumably similar  ${\rm C_3A}$  contents actually differed with RC-332 containing much more crystalline  ${\rm C_3A}$  was considered significant. Each cement led to significant expansion due to sulfate attack (Tables 6, 7) with the one (RC-334) having the smaller amount of crystalline  ${\rm C_3A}$ , and presumably more glassy aluminate, causing more longer-term expansion before any breakage of bars occurred. This suggests that liberation of incorporated aluminate by other phases took longer than the quicker reaction (i.e., <56 days) of crystalline  ${\rm C_3A}$ . These results are shown in Figure 2, also from the 1959 ACI paper.

### Conclusions

- 33. The effect of combined alkali-silica reaction and sulfate attack on concrete or mortar is faster and more destructive than the effect of either reaction by itself.
- 34. When slag or a pozzolan is to be used to mitigate the effect of alkali-silica reaction or of sulfate attack on mortar or concrete, it is preferable that enough advance experimentation be done with this material to determine the optimum amount of it to use for this purpose.
- 35. High potassium content in a cement caused more alkali-silica reaction than did high sodium content.

general, one can predict specimen behavior from a knowledge of materials combinations. For example, the combination of low-alkali and low- $C_3A$  cement RC-333 with limestone or siliceous aggregate with 5 percent quartzite (Mixtures 3, 2) should be satisfactory, and it was through the 16 years of testing. On the other hand, the combination of high- $C_3A$  cement RC-332 with siliceous aggregate and 5 percent quartzite (Mixture 4) should fail, and all of the beams had failed by 1960 after about 5 years of exposure to the marine environment.

- 27. Inclosure 4 is a 1958 petrographic report describing examination of two failed beams (1823, 1850) from the St. Augustine exposure and of the four project cements. Beam 1850 had obviously failed because of deleterious chemical reactions but Beam 1823 showed only negligible reaction and was probably broken by accident during handling. The report concluded that the much higher potassium content of cement RC-332 in Beam 1850 was probably the major explanation for the different behavior of the beams. It also speculated on possible interaction effect of one reaction (sulfate attack) on another (alkali-silica reaction).
- 28. Inclosure 5 is a 1957 petrographic report and memorandum about examination of three failed St. Augustine concrete specimens from a different test program. It is included because it is another example of extensive deterioration of concrete containing a high-alkali and high  ${\rm C_3A}$  cement.
- 29. Inclosure 6 is another petrographic report, written in about 1966, of a failed beam that was returned from St. Augustine after about 9 years of exposure. It had the same high-alkali and high-C<sub>3</sub>A cement (RC-332) and reactive aggregate combination as the earlier failed beam 1850, but this later beam also contained 20 percent fly ash. It appeared that the ultimate fate of this later beam was the same as Beam 1850, but this fate had been deferred but not prevented by the presence of the pozzolanic fly ash. This is not surprising since later work indicated that at least 40 percent of such ash would be required for maximum effectiveness.

### Discussion

30. As indicated earlier, the intent was to make three concrete mixtures that would show maximum effect due to both types of reaction, to make three mixtures that should show no effect from either reaction, to make three mixtures

examination showed some evidence of alkali-silica reaction in most sets of bars, no sign of reaction in the low-alkali and low- $C_3A$  cement RC-333 with chert gravel or this gravel with 5 percent quartzite, and most evidence of this reaction in the bars made with high-alkali and high- $C_3A$  cement RC-332 with gravel and quartzite. There was no sign of sulfate attack in the form of recognizable ettringite.

- 23. Table 6 shows expansion data through 1 year for the 10 mortar mixtures tested in the Lerch test (CRD-C 232)  $^3$  (ASTM: C 452) using all 4 cements. The high-alkali and high- $\mathrm{C_3A}$  cement RC-332 mixture and the low-alkali and high- $\mathrm{C_3A}$  cement RC-334 mixture were both repeated. Reproducibility was probably satisfactory in both cases. The use of 40 percent of either slag with RC-332 was relatively ineffective. While they were more effective with cement RC-334, they still did not reduce expansion to a satisfactory level. The extreme expansion at 1 year of over 1 percent for the low-alkali and high- $\mathrm{C_3A}$  RC-334 was especially noticeable, particularly when compared to 1-year expansion of substantially less than 1 percent for the high-alkali and high- $\mathrm{C_3A}$  cement RC-332. As expected, expansion was lowest when alkali and  $\mathrm{C_3A}$  contents were both low (RC-333).
- 24. Six mortar mixtures were tested in the Lean Mortar Bar Test (see footnote to Section 15). Expansion data for these through a maximum age of 609 days are shown in Table 7. These evaluate the high-C<sub>3</sub>A cements (RC-332, 334) alone and with 40 percent of each slag. As with the other test for sulfate resistance, both cements lead to excessive expansion or breaking of bars with RC-334 bars expanding over 1 percent in less than 1 year. As before, the data indicate that each slag reduces expansion but probably not enough, especially at the longer ages.
- 25. Concretes. Table 8 shows the compressive strength data through 90 days and the static E results through 90 days that were obtained in the laboratory for the 18 concrete mixtures. Mixture B was a repeat of Mixture 6 with 3/4-in. instead of 1-1/2-in. limestone aggregate and cement RC-334. Mixture A was a repeat of Mixture 5 with 19.0-mm (3/4-in.) instead of 37.5-mm (1-1/2-in.) limestone aggregate and cement RC-332. The mixture designations are those used in the book that contained all of the field data.
- 26. Table 9 contains data from Reference I for the beams of these 18 concrete mixtures through the 1970 readings. In addition, the final readings that were made in the laboratory when 15 beams were returned are shown. In

Table 8 (Concluded)

Static Modulus,	x 100(5) 28 Day 90 Day		5.07		6.24	5.84
Static	x IC 28 Day		4.71		5.79	5.51
Compressive Strength,	7 Day 28 Day 90 Day	(C-332	3870		5430	5340
ssive St	28 Day	Sement R	2260 3400		4780	4520
Compres	7 Day	High C <sub>3</sub> A (	2260		3210	2880
Mixture Data	Materials	High-Alkali, High C <sub>3</sub> A Cement RC-332	Natural + 5 percent quartzite,	<pre>30 percent calcined shale (AD-5(3))</pre>	Limestone aggregate, 40 percent RC-296 slaw	Limestone aggregate, 40 percent RC-216(4) slag
	Designa- tion(a)		11		O	Q

The numbered mixtures contained 37.5-mm (1-1/2-in.) nominal maximum size aggregate; the other mixtures contained 19.0-mm (3/4-in.) nominal maximum size aggregate. Each value is the three-round average for nine cylinders (each 6 by 12 in.) (a)

(P)

Table 9

Sonic Data for Concrete Beams Exposed at St. Augustine, Florida

0.121	J	50	5	
1971(f)	113 114	108 105	102 102	
1970 %E %VZ	99 120 113 115 105 116 117 119 116 119	109 109 110 105 108 107 113 108 103 101 112 106	112 105 99 108 105 107 104 107 108 92	
1968 %E %v2	99 114 113 117 105 111 115 116 116 119 112 119	109 110 110 111 108 111 113 104 103 103 112 105	110 101 99 107 105 106 104 108 110 101	
1966 %E %VZ	101 133 114 126 101 132 111 134 115 134 113 137	109 121 108 123 107 125 107 119 107 120 108 119	106 113 103 116 105 116 105 105 105 101	
1964 %E %VZ	110 112 112 113 103 119 107 119 118 116 115 116	109 102 106 106 106 105 107 100 107 99 106 101	110 101 102 101 103 99 108 99 108 95	Ä
1962 %E %VZ	113 122 115 128 105 127 111 134 118 125 114 137	111 123 108 120 106 117 109 116 109 112 108 113	105 109 102 114 107 113 105 113	1 1
1960 %E %VZ RC-333	119 121 119 118 117 119 118 122 119 122 120 123	116 111 112 111 112 114 115 108 116 106 115 108	110 104 109 109 108 105 110 106 108 105	
1	120 115 120 112 124 116 132 113 146 114 139 117	131 109 132 109 117 109 120 102 119 102 120 102	A Cement 125 101 115 101 119 100 121 98 121 98	
1956 %E %VZ , Low C <sub>3</sub> A	109 112 109 108 112 112 111 110 114 111 113 114	107 106 109 109 107 105 107 102 108 98 108 101	11, Low C <sub>3</sub> 104 99 103 89 103 100 104 100 107 98	
Pulse Veloc 1956 1958 fps %v <sup>2</sup> %E %v <sup>2</sup> %E %v <sup>2</sup> Low-Alkali, Low C <sub>3</sub> A Cement	14,880 100 15,150 100 14,975 100 14,705 100 14,535 100	14,370 100 14,370 100 14,450 100 15,060 100 15,060 100 14,880 100	High-Alkali, Low C <sub>3</sub> A Cement 15,060 100 104 99 125 101 14,705 100 103 89 115 101 14,795 100 103 100 119 100 14,795 100 107 98 121 98 121 98 121 98 121 98	14,620 14,970 14,970 14,535 14,880 15,060
%E	00110001	100 100 100 100 100	100	
Coarse(a) Aggregate	Limestone	<pre>!datural gravel</pre>	Natural gravel	Natural gravel + quartz- ite (5 percent)
Fine	Limestone sand	Natural sand	Natural sand	Natural sand
Replacement Material(a) (Pozzolan)	None	None	None	None
Beam No.	1841 1842 1844 1845 1847 1847	1832 1833 1835 1836 1838	1877 1878 1880 1881 1883	
Mixture Designa- tion(e)	c	2	7	-

Table 9 (Continued)

1971 (f) <u>%E %vZ</u> 113 104	133 96	94 104	106 113
1970 2E 2VZ 108 100 106 101 87 100 106 98 111 100 105 99	104 110 126 106 113 103 110 98 130 108 118 99	99 105 114 117 111 114 111 118 121 113 117 116	111 111 114 111 103 107 110 108 112 109 112 103
1968 ZE ZVZ 108 104 106 104 90 107 104 104 111 104 105 103	104 110 126 109 115 107 112 102 133 113	103 112 114 118 111 117 111 115 121 113 117 111	111 109 112 112 101 115 110 109 110 111 112 111
1966 <u>XE</u> <u>XVZ</u> 112 112 109 118 94 113 107 112 111 113 110 111	104 119 124 118 114 115 110 118 134 120 118 114	99 119 116 134 113 133 111 129 114 125 112 127	109 127 113 81 103 120 106 123 108 147 110 135
1964 ZE ZVZ 102 96 106 98 92 100 107 99 109 98	104 105 123 105 113 102 119 93 119 110 122 99	103 106 114 117 113 111 117 112 114 110 112 110	111 103 114 105 107 107 106 107 108 99 112 109
1962 2E 2V2 107 112 108 113 93 114 103 114 107 115 109 110	102 119 119 116 113 114 113 111 125 113 115 112	103 122 114 129 112 128 111 131 114 126 112 125	111 118 114 118 109 123 106 122 108 122 107 122
1960 <u>%E %V2</u> 114 106 115 107 96 110 110 107 111 105	107 109 125 109 119 110 121 107 133 110 121 106 RC-334	107 116 119 120 116 120 117 118 118 116 117 115	122 110 121 110 115 119 115 129 123 116 122 116
1958 ZE ZVZ 122 94 122 101 106 101 116 102 122 100 120 100	131 112 131 105 122 102 123 101 129 110 127 102 A Cement	125 117 130 118 126 116 128 115 127 112 131 112	122 109 115 112 114 113 128 99 115 115
1956 %E %V2 106 97 107 98 108 105 104 102 107 98 108 97	115 102 114 102 109 99 110 98 113 99 110 99 i, High-C.	108 114 110 115 110 113 110 113 108 109 108 109	
Pulse Veloc ZE fps 2v <sup>2</sup> 100 14,705 100 100 14,705 100 100 14,705 100 100 14,880 100 100 14,880 100 100 14,880 100	100 13,735 100 115 102 131 112 100 13,810 100 114 102 131 105 100 14,125 100 109 99 122 102 100 14,370 100 110 98 123 101 100 13,890 100 113 99 129 110 100 14,125 100 110 99 127 102 Low-Alkali, High-C <sub>4</sub> A Cement	100 14,705 100 100 14,205 100 100 14,205 100 100 14,880 100 100 14,970 100 100 14,980 100	100 15,430 100 100 15,335 100 100 14,620 100 100 14,705 100 100 15,060 100 100 15,060 100
Coarse(a) Aggregate Natural gravel + quartz- ite (5 percent)	Natural gravel + quartz- ite (5 percent)	Limestone	Limestone
Fine Aggregate Natural sand	Natural sand	Limestone sand	Limestone sand
Replacement Material(a) (Pozzolan) Fly ash 20 percent	Shale 30 percent	None	None
Beam No. 1904 1905 1907 1908 1910	1895 1896 1898 1899 1901 1902	1868 1869 1871 1872 1872 1874	2544 2545 2547 2548 2550 2550
Mixture Designa- tion(e)	σ	v	۵

Table 9 (Continued)

1971 <sup>(1)</sup> (E. 2 <u>v</u> Z 116 97	711 511	601 901	
105 105 105 105 105 105	116 105 115 106 113 102 102 102 109 98 115 106 1	103 105 101 109 106 105 108 110 104 112 119 117	108 103 112 109 117 108 128 98 107 107 105 108
<u>~</u> , <u>—</u> —	116 110 115 109 115 109 106 109 113 110	105 109 101 113 108 108 108 112 102 109 119 122	107 109 112 112 115 106 134 107 106 111
	112 119 112 116 117 121 107 119 114 142 116 120	103 138 103 126 103 123 106 122 104 127 114 131	105 112 111 113 104 110 143 114 102 111 101 106
. 3.2	131 105 139 102 112 106 102 106 110 103 113 107	122 108 107 112 104 105 108 112 108 109 115 111	107 106 113 106 106 105 146 103 104 110 103 121
	115 124 113 121 114 119 108 119 110 113	105 122 99 124 106 121 108 122 104 127 114 132	109 116 114 121 110 117 162 120 104 126 107 102
, 9/2	121 110 118 113 123 110 122 112 116 113 119 113	RC-332 110 113 110 115 110 112 112 113 108 113	115 115 121 115 117 114 117 112 113 115 105 121
1 00 00	127 104 130 106 130 106 123 105 130 105 129 106	3A Cement 126 106 120 117 126 110 124 113 123 111 124 109	113 109 116 112 111 106 112 109 111 109
1956 %E 202		1, High-C, 105 109 105 109 105 109 105 109 105 109 105 105 109 105 105 105 105 105 105 105 105 105 105	111 104
Pulse Veloc 2E fps. 2V <sup>2</sup> 100 15,530 100 100 15,625 100 100 15,150 100 100 15,150 100 100 15,150 100 100 15,245 100 100 15,245 100	100 15,245 100 100 15,150 100 100 15,150 100 100 15,060 100 100 15,060 100 100 15,060 100	High-Alkali, High-C <sub>3</sub> A Cement RC-332 100 15,060 100 105 109 126 106 110 11 100 14,880 100 105 109 120 117 110 11 100 14,24 100 106 105 126 110 110 11 100 14,795 100 105 109 124 113 112 11 100 14,620 100 105 109 124 109 119 12 100 14,620 100 105 109 124 109 119 12	100 15,245 100 100 15,060 100 100 14,795 100 100 14,795 100 100 14,795 100 100 14,970 100
Coarso(a) Aggregate Limestone	Limestone	Limestone	Limestone
Fine Aggregate Limestone sand	Limestone sand	Limestone	Limestone sand
Replacement Material(a) (Podgolan), RC 198 RC 198 Iurnace slan; 40 percent	RC 216 blast- turnace slag 40 percent	None	None
88.4 8.5 15.7 15.7 15.7 15.7 15.7 15.7 15.7 15	20 20 20 20 20 20 20 20 20 20 20 20 20 2	1859 1860 1862 1803 1865	2535 2536 2538 2538 2539 2541
Mixture Pesigna- roa(e)		î	ਚ

Table 9 (Continued)

	1971(f)	104 103			116 114
	1970 %E %V <sup>2</sup>	105 100 117 99 111 99 108 103 102 101 102 105			129 108 119 109 114 107 115 106 111 97 120 100
	1968 %E %v <sup>2</sup>	103 106 115 103 109 105 108 108 102 99 102 101			126 110 119 110 114 109 115 106 115 103 120 103
	1966 %E %V <sup>Z</sup>	105 111 108 110 105 113 106 114 104 111			121 120 118 116 115 117 113 115 113 110
	1964 %E %V <sup>Z</sup>	105 100 104 98 109 100 108 99 106 95 102 94		43 58 Failed 40 46 Failed	121 106 119 104 115 101 113 101 111 99 113 97
	1962 %E %V <sup>Z</sup>	103 106 107 107 107 110 108 113 103 105 102 109		66 89 53 72 ailed 70	117 117 115 117 113 119 113 115 110 111 115 112
	1960 %E %VZ	107 105 106 104 111 106 111 106 107 101 104 102	Failed Failed Failed Failed	Failed 72 Failed 78 Failed 71 112 105 115 101 69 85 F	122 110 124 113 119 111 118 110 116 106 120 105
	1958 %E %VZ	115 109 113 97 112 100 117 98 114 97 116 99	(b) 124 36 (c) 110 39 77 23 73 26	75 92 100 99 68 88 120 102 129 99 115 96	132 106 130 106 126 103 124 105 127 106 130 100
	1956 %E %v2	105 97 104 98 103 98 104 99 104 98	69 87 66 83 68 87 86 89 67 78 56 79	107 100 106 104 106 100 107 101 108 100	114 102 111 103 1:0 102 113 103 111 102 112 97
	Pulse Veloc ZE fps Zv <sup>2</sup>	100 14,285 100 100 14,450 100 100 14,370 100 100 14,535 100 100 14,880 100 100 14,620 100	100 14,125 100 100 14,370 100 100 14,795 100 100 14,620 100 100 14,620 100 100 14,620 100	100 14,535 100 100 14,555 100 100 14,535 100 100 14,535 100 100 14,705 100	100 13,515 100 100 13,515 100 100 13,890 100 100 13,890 100 100 14,125 100 100 14,285 100
	Coarse(a)	Natural Sravel	Natural gravel + quartz- ite (5 percent)	Natural gravel + quartz- ite (5 percent)	Natural gravel + quartz- ite (5 percent)
!	Fine Aggregate	Natural sand	Natural sand	Natural sand	Natural sand
	Seplacement Material <sup>(a)</sup> (Pozzolan)	None	None	Fly ash 20 per- cent	Shale 30 percent
		1887 1887 1889 1892 1893	1850 1851 1853 1854 1856 1856	1922 1923 1925 1926 1928	1913 1914 1916 1917 1919 1920
1	Mixture Designa- tion(e)	χ	्रं	2	Ξ

~ ~ 1	4	96
1971(f) %E %V <sup>2</sup>	111 10	111 9
1970 %E %VZ	112 103 118 104 116 101 109 100 109 103	114 111 112 110 106 104 110 103 111 108
1968 %E %V2	112 108 118 107 114 105 109 107 111 106	114 108 112 108 108 107 112 107 113 111 116 111
1966 %E %V <sup>Z</sup>	112 143 111 145 113 144 109 144 110 131 111 124	114 123 114 123 109 119 110 117 111 125 113 121
1964 %E %V <sup>2</sup>	114 106 111 106 114 106 109 105 111 106 113 103	118 104 110 104 108 106 110 108 109 107 112 109
1962 %E %VZ	109 119 115 121 109 120 111 117 109 120 113 121	114 120 114 121 112 117 117 117 109 118 112 122
1960 %E %VZ	122 108 130 111 128 111 124 111 127 111 113 109	123 100 114 103 130 105 126 111 127 113 128 115
1958 %E %VZ	111 108 113 107 115 109 111 108 113 108 140 101	150 105 147 105 113 109 123 105 114 108 119 108
1956 %E %VZ		
Pulse Veloc fps	100 15,925 100 100 15,925 100 100 15,530 100 100 15,625 100 100 15,430 100 100 15,430 100	15,335 15,335 15,335 15,430 15,060 14,970
Coarse(a) Aggregate	Limestone	Limestone
Fine Aggregate	Limestone sand	Limestone sand
Replacement Material(a) (Pozzolan)	RC 198 blast- furnace slag 40 percent	RC 216 blast- furnace slag 40 percent
Beam No.	2553 2554 2556 2557 2557 2559 2560	2562 2563 2565 2566 2568 2568
Mixture Designa- tion(e)	U	ਚ

Percentages given are by volume of material replaced.
Returned to laboratory November 1957.
Broken in handling 1958.
Broken in handling 1960.
Broken in handling 1960.
Beams from the numbered mixtures were placed at St. Augustine in 1955; the others were placed there in 1956.
Final reading made after return to laboratory. E E E E E E

CORPS OF ENGINEERS, U. WATERWAYS EXPERI		PETROGRAPHIC REPORT SUMMARY DETAILED		CONCRETE RESEARCH DIVISION P.O. DRAWER 2131 JACKSON, MISSISSIPPI	
<b>SYMBOL</b> : 6510		Effect of Alkali- te Reactivity	SUE	E REPORT	INITIALS:
SERIAL NO WES-1 G-5() WES-1 S-8(3), VICKS-3 G-1(20), VICES-3 MS-10 OM-2 G-2(9)	SOURC		ss. Ten		

1. Samples. Samples of five aggregates, for use in making concrete specimens for exposure at St. Augustine, Florida, were received for petrographic examination. These samples are:

CD No.	Description	Source	
VICKS-3 G-1(2)	Danley Limestone	Near Nashville, Tenn.	
VICKS-3 MS-10	Danley Limestone	Near Nashville, Tenn.	
WES-1 G-5(3)	Natural Chert Gravel	Mear Utica, Miss.	
WES-1 S-8(3)	Natural Sand	Near Utica, Miss.	
OM-2 G-2(9)	Klufa Quartzite	Near Pickstown, S. Dakota	

2. Summary. The coarse and fine aggregates of the Danley limestone are composed largely of medium-dark grey, unweathered, dense, fine-grained limestone with lesser amounts of dolomitic limestone, medium-grained limestone, shaly limestone, chert, gypsum, and calcite (Table 1, 2); the particle shape is predominantly pyramidal. The fine aggregate is excessively dusty, almost every particle has a coating of loose limestone dust.

The natural chert gravel ranges from 99 per cent chert in the 1/2-in. - 3/4-in. sizes to 86 per cent chert in the 3/4-in. - No. 4 sizes (Table 3). The particle shape is blocky to tabular with rounded edges. Approximately three-fourths of the chert is dense with the remainder being either vuggy or porous. A small amount of the chert in this sample is chalcedonic. The natural sand is 83 per cent quartz and 16 per cent chert (Table 4); particle shape ranges from spherical to irregular with sharp or rounded edges. The color is yellowish prey.

The Klufa quartzite is about 70 per cent quartz, 1h per cent opal, and 13 per cent clay and feldspar (Table 5). The sample contains both weathered and unweathered rock; the weathered rock surfaces are partly covered with plants, probably lichens. The color on freshly broken surfaces is light olive grey. It is a very fine-grained, dense rock.

### 6 Incls

- 1. Detailed Report
- 2-6. Tables 1 5

Incl 1

<sup>\*</sup> At least 0.2 percent, probably not over 1.0 percent.

CORPS OF ENGINEERS, U. S. ARMY WATERWAYS EXPERIMENT STATION		PETROGRAPI REPORT SUMMAR	ıY	CONCRETE RES DIVISION P.O DRAWER JACKSON, MISSI	) 2131
<b>SYMBOL</b> : 6510	Armena	Climitect of Alkali- te Reactivity	DAT	E REPORT MITTED: 16 Sep 155	INITIA LS:
SERIAL NO. WES-1 19-50 WES-1 S-F(3), VICES-3 C-1(20), VICES-3 TS-10	SOURC		, Tenr		

l. Test procedure. Pepresentative portions of each lieve fraction of the Danley limertone and of the natural chert gravel and natural sand were examined and classified using either a stereoscopic or netrographic microscope. Acid and scratch tests were also used as an aid in classification. A number of chert particles were crushed and examined in immersion oil to determine the presence or absence of chalcedony by refractive indices. The flufa quartite was examined using X-ray diffraction methods. In addition, several thin sections were made of typical quartite rock; using a point-count technique with the petrographic microscope, fifteen hundred points were examined and classified on a thin section of weathered rock. This process was repeated on a thin section of unweathered rock. These data were used to calculate the composition of the rock.

### 2. Composition.

- a. The coarse and fine aggregates of the Danley limestone are predominantly medium-dark grey, unweathered, dense, fine-grained limestone with lesser amounts of dolomitic limestone, medium-grained limestone, snally limestone, chert, grosum, and calcite. Most of the particles are pyramidal in sname; there is a general increase in amount of tabular particles with decreasing particle size. This sample is very similar to other samples of Danley limestone as described in petrographic reports dated & September 1950 and 2 August 1955. The only real difference being the coating of limestone dust carried on most of the sand particles of this sample.
- b. The natural chert gravel is 99 per cent chert in the 1-1/2-in. 3/4-in. sizes and 66 per cent chert in the 3/4-in. No. 4 sizes. The balance of the smaller size range is largely quartz. The chert is of the dense, vugger, and porous types with the dense chert making up the bulk of it. A small amount of the chert was found to be chalcedonic.
- c. The natural sand is vellowish-grey in color and made up almost entirely of quartz, which is either spherical or irregular in shape.
- d. The flufa quartite is a dense, very fine-grained rock, which is made up of chartz and feldspar grains held together by a matrix of smal and clay. The sample contains both weathered and unweathered rock; some of the weathered rock surfaces are partially covered by plants, probably lichens. Two large, highly-fractured, brown calcite concretions were found on weathered surfaces of the rock. The composition of the weathered and unweathered rock, as determined by a point-count technique, is practically

identical. The color on freshly broken surfaces is light olive grey.

### 3. Pescription of constituents of the Danley limestone.

- a. The fine-grained limestone particles are dark brown to dark grey with smooth surfaces. Tiny dolomite crystals are present in patches in the fine-grained rock or as layers adjacent to it at stylolite contacts in more than one-half of the particles. Stylolites are quite common in this rock.
- b. The medium-grained limestone particles are tan to light brown in color, have smooth surfaces, and are largely free of dolomitic areas and stylolites. The rock consists of spherical colites and angular fine-grained limestone fragments in a matrix of clear calcite. In the finer sand sizes this category was recorded as calcite and fine-grained limestone.
- c. The dolomitic limestone was grouped with the fine-grained limestone category in the coarse aggregate. In the sand it was classified as a separate constituent. It ranges in color from light brown to yellowish green; the particle surfaces have a sugary texture.
- d. The calcite was derived in part from the matrix of the mediumgrained rock and in part from a few random pieces of calcite in the coarse aggregate. Most of the calcite is found as tiny, clear, crystalline rhombs.
- e. The miscellaneous group includes chert, cherty limestone, shaly limestone, gypsum, and iron oxides. The chert is light grey in color and partly chalcedonic. The shaly limestone was derived largely from surfaces exposed by the parting of stylolite seams with crushing.

### 4. Description of constituents of the natural chert gravel and sand.

- a. About three-fourths of all the chert is the dense variety. Color is usually some shade of brown; the particle surfaces are smooth; particle shape is blocky to tabular with rounded edges. A small amount of this chert is chalcedonic.\*
- b. The vuggy chert is brownish in color. The particle surfaces are pitted with depressions of varying sizes, and the particle shape is blocky with rounded edges. Many of these particles are colitic.
- c. The porous chert is usually light in color, tabular in shape, and highly to moderately absorptive.
- d. The quartz of the gravel is spherical in shape with a wide range of colors; that of the sand is spherical or irregular in shape, and most of it is the clear type of quarts.

<sup>\*</sup> All 300+ particles in the 3/4- to 1-in. size were inspected; 12 were selected as possibly chalcedonic. A second inspection was made; 6 more were selected. Five of the 12 and 1 of the 6 (total 6 out of 18) showed chalcedony to the extent of 10 percent on the average of the particle. Thus, 6/300 x 1/10 = 0.2 percent of the sample has been shown to be chalcedony.

### Petrographic Report (concled

- e. The miscellaneous group includes feldspar, iron oxides, and various accessory minerals.
  - 5. Description of constituents of the Klufa quartzite.
    - a. The quartz occurs as clear, spherical grains.
- b. The opal is present in the ock as a clear material which binds all the grains of the rock together. Opal is known to contribute to undesirable reactions in concrete which is made with it. Opal composes II, per cent of both the weathered and unweathered rock.
- c. The feldspar is largely plagioclase. The grains are rounded and unaltered.
  - d. The chert is present as dense, rounded grains.
- e. The miscellaneous category includes clay, altered feldspar, clay covered quartz grains, and various accessory detrital minerals. The clay is of the illitic (non-swelling) type; it is the main constituent of this category and is found thoroughly disseminated throughout the rock. In addition, scattered throughout the rock are cavities up to one-half in. in diameter which are partially filled with a pale green, hard, waxlike material. X-ray analysis proves this material to have the same constituents as the host rock. The clay content of this material is much higher than the clay content of the host rock. The feldspar of this category is partially altered to sericitic mica and will eventually become illitic clay.

Table 1

## COMPOSITION OF VICKS-3 G-1(20) - DANLEY LINESTONE

	In Prac	tions Reta	Fractions Retained on Sieves Shown Below(a)	eves Show	1 Below(4)		
Constituents	1-10	3/4-1a.	Per Cent	3/8-18.	No. 4	Composition by Size Ranges, Per Cent 1-1/2-in 3/4-in. 3/4-in No. 4	Ranges, Per Cent 3/4-in No. 4
Fine-grained Limestone, in Part Dolomitic	29	7.1	83	68	68	78	87
Medium-grained Lime- stone	11	15	<b>20</b>	•	^	13	7
Miscellansous (b)	10	9	6	\$	•	6	9
Total	100	100	100	100	100	100	100
Grading		Samples -	As Individ	ual Percen	itages Reta	of Samples - As Individual Percentages Retained on Sieves Shown Below	le lov
Size Range	1-fn.	3/4-in.	1/2-tn.	•	3/8-in.	No. 4 Passing No. 4(c)	4(c) Total
1-1/2-in 3/4-in.	48.5	45.4	3.6		0.7	0.6 1.2	100.0
3/4-in No. 4	•	2.2	30.7		26.6	32.3 8.2	100.0

Based on a count of at least 300 particles per sieve fraction. Made up of chart, cherty limestone, shaly limestone, calcite, and gypsum. Composition similar to No. 4. Included with No. 4 in calculation of weighted average composition. **3**23

Table 2

COMPOSITION OF VLCKS-3 MS-10 - DANLEY LINESTONE

		In Fractions Retained on Sieves Shows Below(a), Per Cent	Retained	on Steves	Shows Below	(a) Per Ce	nt	In Whole
Constituents	& .	No. 16	<b>%</b> 30	No. 50	No. 100	No. 200	Passing No. 200 No. 200(b)	Sample, Per Cent
Fine-grained Limestone	<b>3</b> 6	62	7.3	76	11	51	37	65
Dolomitic Limestone	93	21	16	14	24	18	13	19
Medium-grained Limestone	91	13	σ	\$	ı	•	•	œ
Calcite	•	•	•	•	4	28	20	'n
Miscellaneous(c)	4	4	8	\$	-	٣	•	æ
Total	100	100	100	100	100	100	100	100

	Total	100.0
Shown Below	Passing No. 200	6.1
ned on Sieves	No. 200	3.9
of Sample - As Individual Percentages Retained on Sieves Shown Below	No. 100	10.5
Individual P.	No. 50	15.4
of Sample - As	No. 30	23.9
Gradine	No. 16	33.6
	No. 8	6.6

Based on count of at least 300 particles in each sleve fraction retained on No. 200. Betimated after examination. Hade up of chert, quartz, shely limestone, and iron oxides.

**323** 

Table 3

COMPOSITION OF WES-1G-5(3) - NATURAL CHERT CRAVEL

9	- 1			מנ				
	-1	3/4-1a.	1/2-10.	3/8-1n.	No. 4	1-1/2-in 3/4-in.	1-1/2-in 3/4-in. 3/4-in No. 4	No. 4
	7.3	78	78	75	62	75	89	
	22	16	11	10	e	19	1	
Chart - Porous	4	<b>5</b>	10	13	13	s	11	
Quartz	•	•		•	22	•	13	
Miscellansous	-4	7		8	•	1	1	
Total	81	100	100	100	100	100	100	
Grading		Semples	-As Indiv	idual Per	centages Retain	of Samples - As Individual Percentages Retained on Sieves Shown Below	n Below	
Size Renge 1-1/	1-1/2-in.	1-1n.	3/4-in.	·	1/2-in. 3/8-in.	Ho. 4 Pass	Passing No. 4(c)	Total
1-1/2-in 3/4-in. 2.	2.0(b)	42.3	45.4		9.5 0.4	0.2	0.2	100.0
3/4-in No. 4		•	3.7	26.1	.1 22.4	43.1	4.7	100.0

Based on a count of at least 300 particles per sieve fraction.
Included with 1-in. material for calculation of weighted average composition.
Composition assumed to be like that of sand. Included with No. 4 in calculation of weighted average **3**20

composition.

Table 4

COMPOSITION OF WES-1S-8(3) - MATURAL SAND

		In Pract	Tone Rete	thed on S	teves Sho	wa Below(	In Practions Retained on Sieves Shown Below(a), Per Cent		In Whole	
Constituents	10. 4	Mo. 8	No. 16	No. 16 No. 30	No. 50	Ио. 50 Ио. 100	No. 200	Passing No. 200(b)	Semple,	, <sub>21</sub>
Quartz	22	54	74	93	97	96	06	06	83	
Chert	78	3	26	٠	~	m	•	٠,	16	
Miscellaneous(c)	•	•	•	-	-	-4	4	\$		
Total	100	100	100	100	100	100	100	100	100	
Č	Crading of Sample . As Individual Parcentages Retained on Sieves Shown Below	e e e e	. Individu	sel Percer	stages Ret	S no bente:	Steves Show	1 Below		
Ho. 4 Ho	Ho. 8	No. 16	No. 30	EO.	No. 50	No. 100	No. 200	O Passing No. 200	l	Total
5.7 14.6		10.8	17.0	*	36.4	13.3	1.3	6.0	م	100.0

Based on count of at least 300 particles in each sieve fraction retained on No. 200. Retimated after examination. Made up of feldspar, from oxides, and various accessory detrital minerals.

**3**20

abundant signs of alkali-aggregate reaction in fairly equal amounts. In addition, it would be expected that the set represented by Beam 1850 would show much more signs of sulfate attack than the set represented by Beam 1823. This examination has shown that the sulfate attack was about as expected, but the amount of attack by alkali-aggregate reaction and the overall condition of the beams were not as expected. The deleterious effects of the reactions that beset Beam 1850 were sufficient to cause its failure after an extremely short exposure time. Beam 1823 showed no deleterious effects from the slight alkali-aggregate reaction seen after identical exposure. The concrete of Beam 1823 appears to be in the same excellent condition at the time of this writing as it was when originally placed at St. Augustine.

17. As previously stated, the only difference in the two beams before their exposure at St. Augustine was that they were made with different cements. The cement used in Beam 1850 is high  $C_3A$  while that used in Beam 1823 is low  $C_3A$  (Table 4). The individual alkali content of the two varies in the following manner:

	RC-331	RC-332
	(Beam 1823)	(Beam 1850)
K <sub>2</sub> 0	0.23%	0.95%
$Na_20$	0.79%	0.37%
Total as Na <sub>2</sub> O	0.94%	1.00%

The difference in  $C_3A$  content could mean that there is a relationship between sulfate attack and attack by alkali-aggregate reaction; one reaction may act as a catalyst or accelerator to intensify the effects of the other when both are present. The difference in  $K_2O$  and  $Na_2O$  contents could mean that potash is a much more active alkali in promoting destructive alkaliaggregate reaction.

18. A recent paper by C. E. S. Davis, \* writing on the comparison of the effect of soda and potash on expansion in cement-aggregate reaction, states that in general, K<sub>2</sub>O caused more rapid reaction and expansion initially, less reaction later, and less total expansion than Na<sub>2</sub>O. Table 3 contains some of the results of the mortar bar tests that were made as part of this program. A petrographic examination was made of the original group of alkali mortar bars shown in Table 3. Two of the sets were made with the same combinations of cements and aggregates as the two beams returned from St. Augustine. The results are given in a report dated 5 September 1956. The bars of both sets showed signs of alkali-aggregate reaction. Those made with the materials used in Beam 1850 were in poor condition and showed more evidence of reaction than those of the other set. The latter was in good condition. There was no formation of sulfoaluminate in either set of mortar bars. It should be noted that the condition of the mortar bars and of the beams is strikingly similar. The difference between the two sets of mortar bars was due entirely to alkali-aggregate reaction in the absence of sulfate attack. The majority of the evidence that has been presented, while not conclusive, seems to support the difference in potash and soda contents of the cements as being the proper explanation for the condition of Beams 1850 and 1823.

<sup>\*</sup> Davis, C. E. S., "Studies in cement-aggregate reaction: XXVI, Comparison of the effect of soda and potash on expansion." Australian Journal of Applied Science, Vol 9, No. 1, pp 52-62 (1958). An abstract of this paper was carried in the Ceramic Abstracts portion of the Journal of the American Ceramic Society, Vol 41, No. 6, p 140 (June 1958).

adhered to the sides of and filled the outer portions of cracks. Tan colloform calcite coated the areas within the tiny circles. The colloform calcite was made up of wedge-shaped crystals in spherulitic arrangement. The calcite-gel mixture formed white, translucent coatings.

### Beam 1823

- 12. This beam, which was made with a high-alkali and low- $C_3A$  cement, was in good physical condition (Photographs 3, 4). There were signs of slight alkali-aggregate reaction but no indication that it has been detrimental to the concrete.
- 13. Exterior surfaces. The outer surfaces were covered with marine shells. The excellent condition of the concrete was indicated by the following observations:
- a. No disintegration, such as edge or corner rounding, pop-outs or surface pits, was visible.
  - b. There was no surface cracking.
  - c. The color of the mortar was light gray.
  - d. The beam gave a clear ring when struck with a hammer.
- e. The beam was extremely difficult to break into pieces, even when a sledge hammer was used.

### 14. Interior surfaces.

- a. Alkali-aggregate reaction. The evidence of reaction was the presence of a little gel in one void and on the surface of one aggregate particle and the condition of the Klufa quartzite particles. The opaline matrix of a few particles had partially vanished leaving groups of loosely bonded sand grains behind. It was possible to scratch, very slightly, the surfaces of most quartzite particles with a steel needle. Fresh Klufa quartzite, as received in the laboratory, cannot be scratched in this manner.
- b. Sulfate attack. The absence of sulfoaluminate crystals indicates that there has been no sulfate attack on this beam.

### Portland Cements

1). The results of the XRD examination of the four portland cements are contained in Tables 4 and 5. Table 6 contains the results obtained by examination of each cement as a powder immersion mount with a petrographic microscope.

### Discussion

16. Consideration of the materials used in these beams and the type of exposure they had would lead one to predict that both sets would show

to its length, and examined with a stereoscopic microscope. Special attention was devoted to the presence of cracks that could be attributed to alkali-aggregate reaction.

- 5. XRD patterns were made of each of the four cements, using the XRD-3D diffractometer with nickel-filtered copper radiation, 4-degree target angle, 49 KVP, and 16 milliamperes at slow scanning speed. The relative amounts of crystalline  $C_3A$  were determined by scaling the 2.70-Å peak of each cement. The apex of the peak was tuned in manually and scaled three times, at each of two locations on each sample surface, and the six values were averaged. The reverter was checked for 95 percent acceptance before and after these peak height determinations; it was adjusted for 93.5 percent acceptance for the background determinations. Background was determined by plotting a straight line through the chart background from 20 to 40 degrees two-theta, and taking the position of the line under the apex of the 2.70-Å peak as the background count.
- 6. Powder immersion mounts of each cement were examined with a petrographic microscope.
- 7. Several photographs were made.

### Results

### Beam 1850

- 8. This beam, made with a high-alkali and high-C<sub>3</sub>A cement, was in poor physical condition. An unusually large and pure sample of alkali-aggregate reaction gel, about 1/2 in. in diameter and 1/8 in. thick, was found on the outer surface of the beam. Table 1 shows results of XRD, chemical analysis, and microscope examination of the gel.
- 9. The outer surfaces were overgrown with marine shells. Cracks were seen on the surfaces (Photograph 1); the mortar was chalky white rather than gray. Striking the beam with a hammer produced a drummy sound, and the beam was easily broken with a hammer.
- 10. Table 2 summarizes the evidence on alkali-silica reaction in Beam 1850. Photograph 2 shows interior cracking. Ettringite was very abundant on the surface of many chert particles, lining old cracks, and in many air voids. It did not completely fill the voids as it sometimes does when it is this plentiful. The sulfoaluminate and gel are what produce the white color of the mortar. During the examination of thin sections, one microcrack in the mortar was noted in which sulfoaluminate had plainly been deposited before the accompanying gel. Sulfate attack may have commenced in this volume at least before alkali-aggregate reaction. Most of the microcracks were empty or the sequence of secondary deposition was not clear.
- 11. Crack sealing materials. Some of the surface cracks were healed (Photograph 1), most commonly by calcite, or by a mixture of gel and calcite. Some of the calcite was light brown or tan and formed as adjoining circles (-1-mm diameter) with tiny vertical walls (<1 mm high). The calcite

Corps of Engineers, USAE	Petrographic Report	P. O. Box 631 Vicksburg, Mississippi
Project Sea-Water Exposur Aggregate Reactivity	e Tests, Alkali-	Date June 1958 ADB

Symbol: 545-6510/71

Serial No.: RC-331, RC-332, RC-333, RC-334, Beam 1850, Beam 1823

### Samples

- 1. A large group of 6- by 6- by 30-in. concrete beams was installed at the St. Augustine Exposure Station during the Fall of 1955. Two of these beams were returned to the Concrete Division (CD) in November 1957, and stored in the moist room until examination was started in March 1958. Beam No. 1850 (RC-332) was one of a group of six which had shown distress by the time of their first inspection in August 1956. Beam No. 1823 (RC-331) was one of a group of six which showed no distress at that time.
- 12. The beams were made with the same mixture proportions, using a natural sand (WES-1 S-8(3)) and chert gravel (WES-1 G-5(3)); 5 percent by volume of the gravel was replaced by reactive Klufa quartzite (OM-2 G-2(9)). The two beams differed only in cement as far as intentional variables are concerned
- 3. The four portland cements used in this program were examined by X-ray diffraction (XRD) with particular emphasis on crystaline tricalcium aluminate content. Two of the cements (RC-332, RC-334) had previously beem examined and the results reported 21 August 1956 in accordance with Memorandum for All Concerned No. 662-D. Sources and serial numbers of the cements are shown below:

CI	Serial No.		Туре
l i	RC-331	Lone Star Cement Corp., Norfolk, Virginia	ΙΙ
i	RC-332	Glens Falls Cement Co., Glens Falls, New York	I
I	RC-333	Permanente Cement Corp., Permanente, California	II
	RC-334	Universal Atlas, Buffington, Indiana	I

### Test Procedure

4. Megascopic examination of the beams began immediately after they were removed from the moist room. The exterior appearance and condition of each was noted; the surfaces were examined for cracks, and each beam was struck several times with a hammer to determine its general physical condition. Portions of each beam were broken into pieces and examined with a stereoscopic microscope. Samples of secondary reaction products from the interior and exterior surfaces of Beam 1850 were examined with a petrographic microscope. A large pure sample of alkali-aggregate reaction gel from the surface of Beam 1850 was examined by XRD and a chemical analysis of it was made. Several thin sections were made from each beam and were examined with a petrographic microscope. A sawed surface was cut from each beam, normal

Table 2 (Continued)

Cesent	RC-331 Hi Alk-Low C3A	531 RC-332 RC-333 LOW C3A B1 A1k-H1 C3A LO A1k-Lo C3A	RC-333 Lo Alk-Lo C3A	RC-331 (B1 A11 + AD-5(3)	(e)1 - Low C <sub>2</sub> A) + AD-3(3)	RC-331 (HI Alkali - Low C <sub>3</sub> A) RC-332 (HI Alk - + AD-5(3) + AD-3(3) HI C <sub>3</sub> A + AD-5(3)
Aggregate		Natural	Natural Gravel + Klufa Quartzite	uartzite.		
Fracture	Bar breaks across most gravel aggre- gate - around most quartzite grains	Bar breaks around most aggregate. Bar easily broken in hand	Bar breaks across larger chert aggre- gate; around smaller aggre- gate.	Bar breaks Bar breaks through and through around aggre-most larger gate - pink aggregate color due to and around calcined smaller Monterey aggregate shale	Bar breaks through most larger aggregate and around smaller aggregate grains	Bar breaks through and around aggregate. Pink color due to calcined Monterey shale
Optical Properties of Gel	Not tested	n is between 1.414 - 1.446;	,	Not rested Not tested	Not tested	Not

Table 2

Examinations of Mortar Bars after Tests - Combinations Made With Reactive Aggregates and Pozzolans

Cement	RC-331 Hi Alk-Low C <sub>3</sub> A	RC-332 H1 Alk-H1 C <sub>3</sub> A	RC-333 Lo Alk-Lo C <sub>3</sub> A	RC-331 (H1 A1 + AD-5(3)	RC-331 (Hi Alkali - Low C <sub>3</sub> A) + AD-5(3) + AD-3(3)	RC-332 (H1 A1k - H1 C <sub>3</sub> A + AD-5(3)
Aggregate		Natural (	Natural Gravel + Klufa Quartzite	uartzite		
Mixture No.	7	7	6	5	9	20
Expansion at						
l yr, per cent	+0.014	+0.130	Zero	+0.00+	+0.020	+0.009
Warping	None	Minor (1 mm)	None	None	Minor (1 mms)	None
Cracking	Scattered	Fine, short,	None	None	None	None
	Micro-cracks	mostly micro-				
Surface Condition	A few incipi-	Some incipi-		As cast		
	ent popouts	ent popouts	As cast	w/few incipi- As cast	As cast	As cast
				ent popouts		
Sulfoaluminate	None	None	None	None	None	None
Exterior Gel	Surfaces heavily	y Surfaces very	No surface	Surfaces	Surfaces	Surfaces slightly
	spotted due to	heavily spotted gal present	ed gel present	very	heavily	spotted due to
	gel liquid - all		(no reaction)	slightly	spotted	dried gel liquid
	dry; mostly	liquid - all		spotted	with clear	
	clear; some	dry; mostly		w/gel	and some	
	paque	gel clear; some			white gel	
		white,opaque gel				
Interior Gel	Some voids	Many voids	No interior	No interior	Many voids	Some voids
	partially	lined and	gel present	gel present	lined and	have alight
	lined with	partially	(No reaction)		filled w/gel	amount of gel
	White gel.	filled w/white			(partially)	lining them
		861				
	w/white gel					

# Examinations of Mortar Bars after Test - Combinations Made With Unreactive and Mildly Reactive Aggregates

Cement	RC-331	RC-331 (Bigh Alkali - Low CaA)	C3 <b>A</b> )	RC-333 (	RC-333 (Low Alkalt - Low C3A)	A).
Aggregate	Manufactured Limestone Sand	Natural Quartz-Chert Sand	Crushed Chert Gravel	Manufactured Limestone Sand	Natural Quartz-Chert Sand	Crushed Chert Gravel
Mixture No.	1	2	3	10	11	12
Expansion at	900-0+	+0,007	Zero	Zero	+0.002	+0.03
Warping	None	None	None (Bar 5 slight)	None	None	None
Cracking	Mone	None		None	None	None
Surface Condition	As Cast	As Cast	ast	As Cast	As Cast	As Cast
Sulfoeluminate	None	None		None	None	None
Exterior Gel	Scattered gel	Scattered gel	pots	Two gel	No surface	No surface
	spots; both	spots; both	or white	spots round on her 6:	get present	Ret present
	liquid and	liquid and	some (not	rest are		
	opaque white	opeque white	all) bars	clean		
	se1	gel. More	•			
	)	numerous than				
		in Mixture 1				
Interior Gel	Gel filled	Very few voids	No interior	Very few	Very few voids	No interior
	void in Bar 6	are partially	gel present	voids have	have gal lining	gel present
	next to chert	filled with clear		thin gel		
	that may not	liquid and opaque		lining		
	belong to this	white gel. Liquid				
	aggregate. None					
	other found in	material.				
ļ	six bars examined.	ed.				
Fracture	Bar breaks	Bar breaks	Bar breaks	Bar breaks	Bar breaks through	
	through aggregat	gate through aggre-	through aggre-		larger aggregate	Across most
	mostly.	gate mostly.	gate mostly.	and around	and around smaller chert pebbles.	chert pebbles.
				aggregate.	rounded quartz	
					B. C. Line	

SUBJECT: Report of Petrographic Examination of Morter Bars

was clear, if liquid, and white or clear, if dried. The interior-void gel was always dry and usually a combination of clear and white with the clear material usually in contact with the sides of the voids. The gel from combination 7 is amorphous; its refractive index is between 1.414 - 1.446.

- 8. The following remarks apply only to the set of bars from combination 7 (high-alkali, high  $C_3A$  cement with reactive aggregate):
  - a. There was a great deal of alkali-aggregate reaction.
  - b. Fine cracks were visible on the surfaces of the bars.
  - c. The bars were physically weak and could be broken easily by hand.
- d. Expansion after one year was greater than one-tenth of one per cent.
- 9. The bars of all combinations except those of No. 7 were essentially in good condition.
- 2 Incl
  Tables 1, 2

CORPS OF ENGINEERS, U. S. ARMY

OFFICE OF THE DIRECTOR

WATERWAYS EXPERIMENT STATION

VICKSBURG MISSISSIPPI

REFER TO SYMBOL WESCI

E THREST IR WATERWAYS EXPERIMENT STATION CONTROL OF SAMMY POUR BOX FOR MISSISS PPE

AT TESS REPORT TO

5 September 1956

SUBJECT: Report of Petrographic Examination of Mortar Bars

PROJECT: Exposure of Specimens & St. Augustine

(Job 6510, Memo: 662-A)

FROM: A. D. Buck through K. Mather and B. Mather

TO: C. H. Willetts

- 1. Twelve sets of mortar bars containing the combinations exposed at St. Augustine to determine the effect on alkali-aggregate reactivity of C<sub>3</sub>A content have been examined and the results are shown on Tables 1, 2.
- 2. Six combinations (1, 2, 3, 10, 11, 12) contained aggregates believed to \(\frac{1}{2}\): unreactive or slightly reactive. Table 1 indicates that the high-alkali cement combinations developed a little more reaction than the low-alkali cement combinations.
- 3. Three combinations (4, 7, 9) contained reactive aggregates, two with high-alkali cements (4, 7) and one with low-alkali cement. The two with high-alkali cement both reacted. The one with low-alkali cement reacted less than any other combination except 12.
- 4. Three combinations (5, 6, 8) contained reactive aggregate and pozzolan. All three showed some signs of reaction; the two combinations with Monterey shale showed less reaction than the one with fly ash.
  - 5. There was no formation of sulfoaluminate in these bars.
- 6. By idence of alkali-aggregate reaction was found in all bars except those of combinations 9 and 12 (low-alkali, low-C<sub>3</sub>A cement). The reaction was extremely slight in the bars of the two sets made with low-alkali cement which did react.
- 7. The evidence for alkali-a ggregate reaction was in the form of gel in combinations 1, 2, 3, 10, 11, 6, and 8 and in the form of gel, cracks, and incipient popouts in combinations 4, 5, and 7. The gel was found on the bar surfaces and lining or filling interior voids or both. The surface gel

Table 2

	]	Methods of Iden	tification	l	
Samples	X-ray Diffraction	Petrographic Microscope	Acid Test	Phase Diagram	Composition of Sample
RC-216(4)	Melilite Calcite Quartz	Glass Nelilite Calcite Quartz	- Calcite	Melilite	Glass > 90% Melliite Calcite(a) Quartz(b)
RC-296	- Calcite Quartz	Glass Calcite Quartz	- Calcite	: :	Glass > 90% Calcite(a) - Major Quartz(b) - Minor

<sup>(</sup>a) Calcite is a common surface alteration product of finely ground quenched slags.
(b) Quartz is a common contaminant of slags.

Table 1

		Calculation from Ch	•
Samples	X-ray Diffraction, Counts per Second	l'er Cen Standard Method(a)	Swayze's Method(h)
RC-332	195	14	9.9
RC-334	100	13	10.2
RC-336(C)	No peak	2.2	2.2
RC-337(C)	125	10.6	5.2
RC-338(C)	150	11.6	10.9
RC-339(C)	130	8.7	8.1
RC-340(C)	215	13.3	12.1
RC-341(C)	190	12.4	8.9
RC-342(C)	200	10.5	4.5
RC-345(C)	130	i2.3	7.4

 <sup>(</sup>a) Note 2, Table I, Fed. Spec. SS-C-192a (CRD-C 200-54).
 (b) Swayze's Method: 1.276 (Wt of Fe<sub>2</sub>O<sub>3</sub>) = Wt of Al<sub>2</sub>O<sub>3</sub> in C<sub>6</sub>A<sub>2</sub>F. Total Al<sub>2</sub>O<sub>3</sub> - Al<sub>2</sub>O<sub>3</sub> in C<sub>6</sub>A<sub>2</sub>F = residual Al<sub>2</sub>O<sub>3</sub>.
 2.55 (Al<sub>2</sub>O<sub>3</sub> residual) = C<sub>3</sub>A. (Am. Jour. Sci., 244, 1946, ρ ο4).

Petrographic Report (Cont'd) <u>Symbol</u>: 6510 <u>Serial No.</u> RC-332,334, (CW 603) RC-216(4), RC-296

Date: 21 August 1956

b. Blast-furnace slags. Examination of these two slags (Table 2) indicated that each is essentially identical to previous samples from the same sources. Therefore, there is every reason to expect behavior similar to that of their counterparts in the blended cement and portland blast-furnace slag cement programs. Neither of these slags contains any crystalline C3A; no blast-furnace slag made under normal conditions should contain any crystalline C3A. RC-296 was more efficiently quenched than RC-216(4).

CORPS OF ENGINEERS, U. S. ARMY
WATERWAYS EXPERIMENT
STATION

PETROGRAPHIC REPORT

CONCRETE RESEARCH
DIVISION
P.O. DRAWER 2131
JACKSON, MISSISSIPPI

	PROJECT: Sea-water Exposure Tests	DATE REPORT SUBMITTED: 21 August 1956	INITIA LSI
SERIAL NO: RC-332, 334; RC-216(4), RC-296	SOURCE: RC-332 - GI Univ. Atlas, Buffing	lens Palls Cement Co.; I ston, Ind.; RC-216(4)	- Birmingham

1. Samples. The samples described below have been examined:

Serial No.	Class of Material
RC-332 RC-334 RC-216(4) RC-296	Type I, high-alkali, high C3A, portland cement.  Type I, low-alkali, high C3A, portland cement.  Water-quenched blast-furnace slag.  Water-quenched blast-furnace slag.

2. Test procedure. X-ray diffraction patterns were made of each sample, using the XRD-3D diffractometer with nickel-filtered copper radiation, 4-deg target angle, at 49 Kvp, 16 ma, slow scanning speed. The relative amounts of C3A in each cement were determined by scaling the 2.70-8 peak. The spex of the peak was tuned in manually and scaled three times, at each of three locations on each sample surface, and the nine values averaged. Background was determined by plotting a straight line through the chart background from 20deg to 40 deg 2-theta, and taking the position of the line under the apex of the 2.70-% peak as the background count. The clinkers of the cements in the portland blast-furnace slag cement program were re-examined by this procedure. Values reported in Table 1 are average peak heights minus background. The slag patterns were compared with patterns of slags from the same sources examined previously. In addition, the slags were examined with a petrographic microscope; tests for magnetic materials and for reactions in dilute hydrochloric acid were made. The major oxides, CaO, Al2O3, SiO2, and MgO were recomputed to 100 per cent from the chemical analyses, and the recalculated compositions plotted on the appropriate phase diagrams to compare the constituents identified with those expected(1).

### 3. Results.

a. Portland cements. Table 1 compares crystalline  $C_3A$  in these cements and in the PBFSC clinkers, as estimated by diffraction and by calculation from chemical analyses. The difference in amount of crystalline  $C_3A$  in RC-332 and RC-334 as determined by the X-ray method is regarded as significant, and it is expected that the behavior of these cements should reflect this difference whenever the crystalline  $C_3A$  content is a primary factor in affecting behavior.

<sup>(1)</sup> E. P. Osborn et al. "Optimum Composition of Blast-Furnace Slag as Deduced from Liquidus Data for the Quaternary System CaO-MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>." Journal of Metals, pp 3-15, 1954.

Table 5

COMPOSITION OF ON-2G-2(9) - KLUFA QUARTZITE

Constituents	Weathered Rock Per Cent(a)	Unweathered Rock Per Cent(a)
Quartz	70	67
Opal	14	14
Feldsper	7	5
Miscellaneous(b)	6	11
Chert	3	3
Total	100	100

- (a) Determined by counting 1500 points on a thin section of typical rock using a point-count technique and a petroscaphic microscope.
- (b) Consists of illitic clay, altered feldspar, clay covered quartz, and various accessory detrital minerals.

Composition of Alkali-Aggregate Reaction Gel from the Surface of Beam 1850 (a) Table 1

		Methods of Examination	
Chemical Analysis	is		
	percent	X-Ray Diffraction	Microscope
Moisture loss at 105° C	5.22	Sample was 95 to 98 percent	Gel was completely amorphous with R.I. between 1,440-1,480.
additional moisture ross at 200° C		cite and quartz	The majority was close to 1.460.
Additional moixture loss at 300° C	None		A small amount of calcite was identified.
Total moisture loss	8.31		
Si0,	85.91		
Na <sub>2</sub> 0	2.41		
K <sub>2</sub> 0	09.0		
cão	1.25		
Total	98.48		

This was one patch of white, porcelaneous to powdery gel of unusual size and purity. The spot was about 1/2 in. in diamter and 1/8 in. thick. The sample was further purified by hand picking under a stereoscopic microscope before the X-ray examination and chemical analysis were made. (a)

Table 2
Results of Examination of Beam 1850

Secondary Deposits on	Color of Aggregate	Reaction Gel Mortar Particles	us No color	or clear. Found on grada- sulfoalumi-		- jacent	gate surfaces, satu- to surfaces of	-	and sealing surface the en- particles.		ï		petrographic micro- showing	scope, one clear and extensive	amorphous with R.I. reaction.	en 1.480-1.500;	The other very slightly	crystalline, has low	birefringence and	sweeping extinction	with R.I. between	1.460-1.544, light tan	in plane light.
	Type of	all	•	-	through beam			rtzite ratin		around crack	almost of in				parti- amorp	_	The o	cryst	biref	sweep	with	1.460	in pl
Reaction		Aggregate Fra	Not Beam	observed broke	thr	the	Klufa	dua	but	aro	alm	a11	the	chert	par	cles.							
1	I	Reacted Aggregate	No evidence of	reaction by fine	aggregate or	gravel. Much	of Klufa quartz-	ite reacted;	opaline matrix	dissolved leaving	a residue of un-	consolidated	sand grains.										
		Interior Cracks	Cracking seen	on the outer	surfaces con-	tinued inside	the beam.	Minor cracking	in some chert	particles. No	cracks seen	that were con-	tinuous from	mortar to ag-	gregate or vice	versa.							
		Exterior Cracks	Visible crack-	ing seen on	top, bottom,	and one side	of beam. The	outer 1/8 to	1/4 in. of	these cracks	are often	healed with a	mixture of cal-	cite and gel	which may con-	tain small	amounts of	Ca(OH),. The	The cracks range	up to 1 mm in	width.		

Table 3

Partial Results of the Mortar Bar Test for Potential Alkali-Aggregate Reactivity

		( - )	A	verage S	et Expans	Average Set Expansion, percent	ent
Cement		Aggregate (4)	8 day	28 day	28 day 84 day 196 day	196 day	364 day
RC-332, Hi Alk, Hi C3A	Hi C3A	Natural gravel + Klufa quartzite	0.012	0.022			0.130
RC-331, Hi Alk,	Lo C3A	Natural gravel + Klufa quartzite	0.001	0.004	0.011	0.010	0.014
RC-333, Lo Alk,	Lo C <sub>3</sub> A	Natural gravel + Klufa quartzite	0.001	-0.003	-0.002	-0.004	000.0
71	Additional	Additional Test Data Developed Due to Results Shown Above by RC-332 + RC-331	Above b	y RC-332	+ RC-33	1	
RC-332		Same as above	0.010	0.028	0.070	0.105	0.109
RC-331		Same as above	0.001	0.014	0.025	0.054	0.063
RC-332		Pyrex glass	0.161	0.288	0.298	0.311	0.320
RC-331		Pyrex glass	0.075	0.257	0.321	0.344	0.358
	Partial Res	Partial Results of the Lerch Mortar Bar Test for Potential Sulfate Resistance	tential	Sulfate	Resistand	je	
Lo Alk,	Hi C <sub>3</sub> A	Standard Ottawa sand	0.054	0.142	0.354	1.762	1.772
RC-332, Hi Alk, F	Hi C3A	Standard Ottawa sand	0.051	0.124	0.346	0.348	0.354
Hi Alk,	Lo C3A	Standard Ottawa sand	0.024	0.047	0.073	0.094	0.108
Lo Alk,	Lo C3A	Standard Ottawa sand	0.013	0.025	0.036	0.044	0.056

<sup>(</sup>a) Five percent of the gravel, by weight, was replaced by quartzite.

		X-Ray Intensity,	
CD Serial No.	C <sub>3</sub> A Calculated from Chemical Analysis	counts/second on 2.70-A Peak	Peak Location, in Angstrom Units
RC-332	14.2%	310 <sup>(a)</sup>	2.704
RC-331	5.4%	235	2.710 <sup>(b)</sup>
RC-334	13.4%	205 <sup>(a)</sup>	2.699
RC-333	4.4%	Not detected	

(a) The ratio of 310/205 is about 3:2. The values given in the previous report were 195/100, or about 4:2. The change in intensity values is due largely to changes made in the equipment during the interim. The agreement between the two ratios is considered quite satisfactory.

(b) This is two peaks, one at 2.704 due to  $C_3A$ , one at 2.720 is a substituted calcium silicate. The 2.704 peak is stronger than the 2.699 peak of RC-334.

Calcium Sulfates in Four Portland Cements Table 5

Calcium Sulfates by X-Ray Diffraction	Gypsum (a) Hemihydrate of Gypsum (b) $(CaSO_4 \cdot 2H_2O)$ $(CaSO_4 \cdot 0.5H_2O)$ Anhydrite (a) $(CaSO_4)$	Not detectable Not detectable Not detectable	Not detectable Not detectable Not detectable	Not detectable Not detectable Definitely identified	Not detectable Not detectable May be present
1 1	$\frac{\text{Gypsum}(a)}{(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})}$	Not detectable			
	SO <sub>3</sub> Content, by Chemical Analysis	1.95%	2.11%	2.13%	2.14%
	CD Serial No.	RC-331	RC-332	RC-333	RC-334

(a) Experience has indicated that these materials may be identified when they are present in amounts as small as 1 to 2 percent.
 (b) A larger amount of this material is necessary for recognition than for either of the other two. It has not been definitely identified in any portland cements examined by this laboratory.

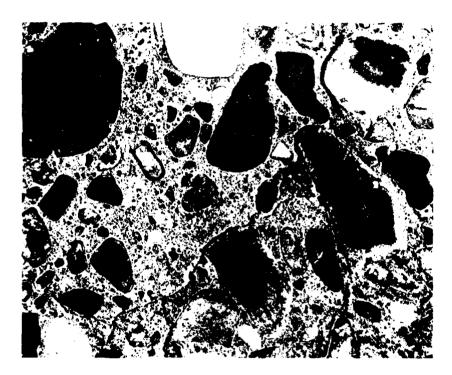
Data on Calcium Silicates Obtained by Microscope Examination of Four Portland Cements Table 6

	<b>E</b>	Belite Phase			
			Estimated	Alite	Alite Phase
	Average Crystal	Maximum Crystal	ш.	Average Crystal	Average Crystal Maximum Crystal
	Size, Longest	Size, Longest		Size, Longest	Size, Longest
Cement	Diameter(a)	Diameter	C2S Content	Diameter(a)	Diameter
RC-331	40 microns	40 microns	First	20 microns	52 microns
RC-332	Not determined	50 microns	Fourth	40 microns	62 microns
RC-333	40 microns	50 microns	First	20 microns	70 microns
RC-334	<20 microns	20 microns	Third	20 microns	46 microns

<sup>(</sup>a) Value was estimated after several grains had been measured.



Outer surface of Beam 1850 (X1.5) showing cracks and marine shells. Some of the healed cracks are shown by the inked lines.



Sawed surface of Beam 1850 (X1.5) showing internal cracks.



Outer surface of Beam 1823 (X1.5) showing marine shells. Note absence of cracks.



Sawed surface of Beam 1823 (X1.5). Note absence of internal cracking.

### CORPS OF ENGINEERS, U. S. ARMY

OFFICE OF THE DIRECTOR

### WATERWAYS EXPERIMENT STATION

VICKSBURG, MISUSSIPPI

SEFER TO SYMBOL \_WESCI\_

THE DIRECTOR WATERWAYS EXPERIMENT STATION CORPS OF ENGINEERS, U.S. ARMY P.O. BOX. 831. VIOUSE FO. WIESTSTIPP.

ADDRESS HEPLY TO:

14 May 1957

MEMORANDUM FOR THE FILES:

SUBJECT: E-Series Columns, St. Augustine, Florida

1. Attached is a petrographic report dated 10 May 1957 giving data on and results of examination of three columns as follows:

		C	ement	Con	ncrete
Column	Year "Failed"	Na <sub>2</sub> 0 Eq.,7	Calculated C3A, %	Color of Mortar	Evidence of Deterioration
E-6-H	1950	0.60	4.6	Gray	None
E-9-H	<b>19</b> 50	0.53	4.6	Gray	None
E-32-H	1948	1.02	13.6	Yellowish	Large amount of sulfoaluminate, abundant alkali-reaction gel

- 2. The significance of these findings is:
- a. Only the concrete made with the high-alkali, high-C<sub>3</sub>A cement shows evidence of deteriorative processes that led to failure; the other two "failed" specimens may represent breakage due to handling.
- b. The examination of E-32-H provides one of the first examples of distinct alkali-aggregate reaction involving the natural aggregate from Long Island, New York; and also is an example of concurrent alkali-aggregate reaction and sulfate attack deterioration.
  - 3. It is recommended that these findings be cited in:
- a. The next general report on natural weathering in the series of which TM 6-226 (Report No. 5), May 1954, is the latest.
- h. In the report of the investigation now in progress, "Exposure of Specimens at St. Augustine, Florida" (Memo. No. 662).

Incl
Porm 557

BRYANT MATHER, Chief Special Investigations Branch Concrete Division

Incl 5

CORPS OF ENGINEER WATERWAYS EXP	PERIMENT	PETROGRAPH REPORT	IIC	CONCRETE DIVI: P.O. DRAW JACKSON, N	SION VER 2131
<b>SYMBOL</b> : 6510	PROJEC Expos	CT: Sea-water ure Tests		E REPORT MITTED: 0 May 1957	INITIA LS:
SERIAL NO: E-6-H, E-9-H, E-32-H	SOURC	E-Ser	ies	Columns tine, Florida	

1. Samples. Three 6-in. by 6-in, by 48-in, concrete columns from the series made as part of the Cement Durability Program, (1) which had failed during sea-water exposure tests at St. Augustine, Florida, were returned to the laboratory in August of 1956 for examination. The examination was conducted to determine, if possible, why the columns had failed, and any unusual features which might be noted. The columns were identified as E-6-H, E-9-H, and E-32-H. Each column contained a different cement; each cement was represented at the exposure station by a set of three columns. The same mixture proportions, and coarse and fine aggregate from one source, were used in all the concrete, so that the only variable under test was the cement. The mixture proportions used in making these specimens were as follows:

		Proportions by	W/C	C. P.	Nominal Slump	
	Fine	Coarse Aggregate		g <b>a</b> 1/		
Cement	Aggregate	1 2-in No. 4	1-in 1/2-in.	bag	си у <b>d</b>	in.
1	2.53	1.80	2.71	6.0	5.1	2

The specimens were made during the summer of 1940 and placed at the exposure station in early October of that year. The following table gives a summary of the durability factors for the sets concerned during the years 1940-1956.(2)

Table 1

	_		DFE					
Year								
Column	1942	1946	1948	1950	1952	1954	<u>1956</u>	
E-6-E	114	119	120	121	115	118	116	
ĸE-6-H	115	122	111	Pailed	-	-	-	
E-6-K	112	126	123	120	119	114	120	
£-9-E	114	122	Broken in Handling	-	-	•	-	
жЕ-9-Н	117	131	105	Failed	-	-	-	
E-9-K	113	121	127	118	117	114	112	
E-32-E	124	125	Failed	-	-	-	-	
×E-32-H	127	126	Pailed	-	-	-	-	
E-32-X	127	128	Failed	-	•	-	-	

<sup>(1)</sup> First Interim Report, Cement Durability Program, June 1942.

<sup>(2)</sup> Taken from Table 3 of Report No. 5, Technical Memorandum 6-266 and from unpublished data.

Petrographic Report (Continued) Symbol: 6510

10 May 1957

Serial No.: E-6-H

E-9-H,

E-32-H

Some data for the cements that were used is shown in the following table:

Table 2

	Clinker Serial	Type Based	Total	C3A Content, X		
Cement Serial No.		on Existing Federal Speci- fications in 1942	Alkali Content, Expressed as Na <sub>2</sub> 0,%	Calculated from the Chemical Analysis	Determined by Micrometric Analysis of Clinker	
E-6(KC-6)	£-6	II, plain	0.60	4.6	0.1	
E-9(RC-9)	E-9	II, plain	0.53	4.6	0.3	
E-32(RC-29	) - <sup>(a)</sup>	I, air-entrai	ning 1,02	13.6	_(4)	

<sup>(</sup>a) No E-32 clinker was sampled.

2. Test Procedure. The condition and appearance of the specimens wassobserved. The ring produced by striking the concrete with a hammer was observed. The toughness of the concrete was checked by using a hammer to break up portions of each specimen. Since the outer surfaces were covered with shells, etc., from the sea, the detailed examination was made on concrete from the interior of each column. Fresh broken and saved surfaces of each specimen were examined using a stereoscopic microscope. A saw cut was made normal to the length of each column about six inches from the end; a series of adjoining thin sections were then made across the mid-portion of each surface from one side to the other. A petrographic microscope was used to examine these sections and to check reaction products found in the concrete. The companion surface to each of those from which the thin sections were made was examined at 45% and at 60% with a stereoscopic microscope for the presence of microcracks. A point-count technique with a 3/8-in, point spacing was used. A General Electric XRD-3 diffractometer employing nickel-filtered copper radiation at 49 kilovolts and 16 milliamperes was used to obtain diffraction patterns of the clinkers of E-6 and E-9 and of the mortar from column E-32-H.

### 3. Results.

a. General Statement. Examination of column E-32-H indicates that it is entirely reasonable and to be expected that it and the remainder of the set failed during test. The failure was due to the damage suffered through the mechanism of alkali-aggregate reaction and the formation of excessive amounts of calcium sulfoaluminate. On the other hand, examination of columns E-6-H and E-9-H has revealed no obvious reason or reasons for

Petrographic Report (Continued) Symbol: 6510

10 May 1957

Serial No.: E-6-H,

Е-9-Н, Е-32-Н

their failure. These columns would still be in Florida undergoing test were it not for the single break in each which was responsible for their return to the laboratory.

### b. General Observations.

- (1) The mortar of column E-6-H and of E-9-H is medium gray in color; there is no sign of alkali-aggregate reaction; some calcium sulfoaluminate is present in voids and also may be found occasionally where mortar and aggregate meet. The concrete appears to be in good condition.
- (2) The mortar of column E-32-H is very, very light yellowish gray in color. This color is probably associated with secondary reactions, but it may be due to the color of the cement itself. There is a large amount of calcium sulfoaluminate in this specimen; it is found in voids and in aggregate sockets or on aggregate surfaces. Alkali-reaction gel is abundant in voids, on aggregate surfaces, and in mortar. The concrete of this specimen is not in as good condition as the concrete in E-6 and E-9.
- (3) Examination of the thin sections gave results consistent with the observations made with the stereoscopic microscope. In addition, the sections showed that the depth of carbonation of the concrete surfaces was less than one-half inch.
- (4) There are essentially no cracks, large or small, in the interiors of specimens E-6-H and E-9-H. The debris and shells on the outer surfaces made it impossible to examine them for cracking with any success.
- (5) No unusual features were present in the X-ray patterns of clinkers E-6 and E-9. The amount of crystalline  $C_3A$  in each of these two clinkers appears to be below five per cent; this was determined by using the X-ray method reported in Miscellaneous Paper No. 6-201, March 1957. These results are in rood agreement with those shown in Table 2 of this report. No sample of the cement or clinker of E-32 was available for study. The pattern of the mortar of E-32-H confirmed the findings which had been made by visual and microscopic examination of it.

Corps of Engineers, USAE Waterways Experiment Station Petrographic Report

Concrete Division P. O. Drawer 2131 Jackson, Mississippi

Project Sea Water Exposure,
Alkali-Aggregate Reactivity

Date About September 1966 AB, BA

### Sample

- 1. One 6- by 6- by 30-in. concrete beam described below was examined as directed by Memorandum for All Concerned No. 662.
- 2. The beam was installed at the St. Augustine Exposure Station during August 1955. It failed in 1964 and was received at the Concrete Division (CD) for examination in August 1966. The beam identification number was either 1926 or 1928, but positive identification was impossible due to the presence of numerous marine shells covering the entire surface of the beam. Beams 1926 and 1928 were two of a group of nine beams made to the same mixture proportions using high-alkali and high- $C_3A$  cement (RC-332), natural sand (WES-1 S-8(3)), natural gravel (WES-1 G-5(3)) containing 5 percent Klufa quartzite (OM-2 G-2(9)) and 20 percent fly ash as a cement replacement material. The cement factor of this set was between 4.5 and 5.8 bags/yd $^3$ , water/cement ratio was 0.5 by weight, air content was 5.0  $\pm$  0.5 percent, and the slump was  $2-1/2 \pm 1/2$  in. Six of the beams were sent to the St. Augustine Exposure Station and three stored out-of-doors at the CD.

### Test Procedure

- 3. The surface of the beam was examined for cracks and struck several times with a hammer. A photograph was taken to show the effects of reactions. The beam was broken and portions of it were examined with a stereomicroscope.
- 4. The beam was sawed normal to its length to expose a fresh surface and several thin sections were made from this surface. Special attention was devoted to cracks and possible alkali-aggregate reaction in selecting areas for thin sections. The thin sections were examined with a petrographic microscope on a comparative basis with sections already made from Beams 1850 and 1823. Beam 1850 had shown heavy alkali-aggregate reaction and sulfate attack while Beam 1823 had shown only slight alkali-aggregate reaction when examined in November 1957. Beam 1850 differed from Beam 1926 or 1928 in that it did not have fly ash as a cement replacement material. Beam 1823 was made with a different cement and contained no fly ash.
- 5. The beam, 1926 or 1928, was also compared with Beams 1924, 1927, and 1930 which have the same mixture proportions. These three beams were installed outdoors at the Concrete Laboratory during September 1955. The beams were compared by visual appearance and by determination of relative E.

### Results

6. This beam, made with a high-alkali and high- $C_3\Lambda$  cement (RC-332), was in poor physical condition as a result of alkali-silica reaction and probable sulfate attack.

- 7. The center of the beam was deeply and severely cracked around all four sides and had lesser cracks around all four sides at one end of the beam. The cracks perpendicular to the centerline of the beam were connected by lesser cracks running parallel to the length of the beam.
- 8. The beam was broken in the center where the most severe cracking had occurred. The beam had been penetrated nearly to its center by sea water and had a dark yellowish green color like the outer surface of the beam. A white and powdery reaction product was quite evident around the aggregate particles and in lesser amounts on the surface of the mortar. One reaction product and possibly two were confirmed under the stereomicroscope.
- 9. Freshly sawed surfaces of the beam revealed numerous fine cracks throughout the beam which generally propagated from aggregate particles which had been subjected to alkali-aggregate reaction. The reaction was especially noticeable in the reactive quartzite particles where the opal cementing agent had been dissolved leaving individual quartz particles loose or in a spongy mass. Photograph 1 shows three reacted quartzite particles where the core of the particles was unaffected. Other signs of reaction included the obvious expansion of the beam, gel found in cracks and other voids, and the reaction products on the surface of many chert particles.

### Summary

- 10. Consideration of the materials used in this beam and of the type exposure it had been subjected to would lead one to predict that alkali-silica reaction was to be expected. It would also be expected that sulfate attack through the medium of sea water would occur.
- 11. The other three beams of this set, exposed outdoors at the Jackson, Mississippi, Suboffice showed no signs of distress except for a very fine crack on one end of Beam 1927. The crack obviously was so small that it did not affect its 1966 percent E reading which was 100, or else the cracking occurred after the reading had taken place. The crack in Beam 1927 may be the beginning of alkali-silica reaction proceeding slowly as would be expected without the aid of sulfate attack and with only occasional and limited amounts of water.



Sawed surface of Specimen 1926 or 1928, X1. Note the many cracks which are visible; many of these are filled with secondary deposits. Three reacted quartzite particles are marked with an X; these particles illustrate cases where the core of the particles was unaffected by the reaction

## END

### FILMED

5-85

DTIC